

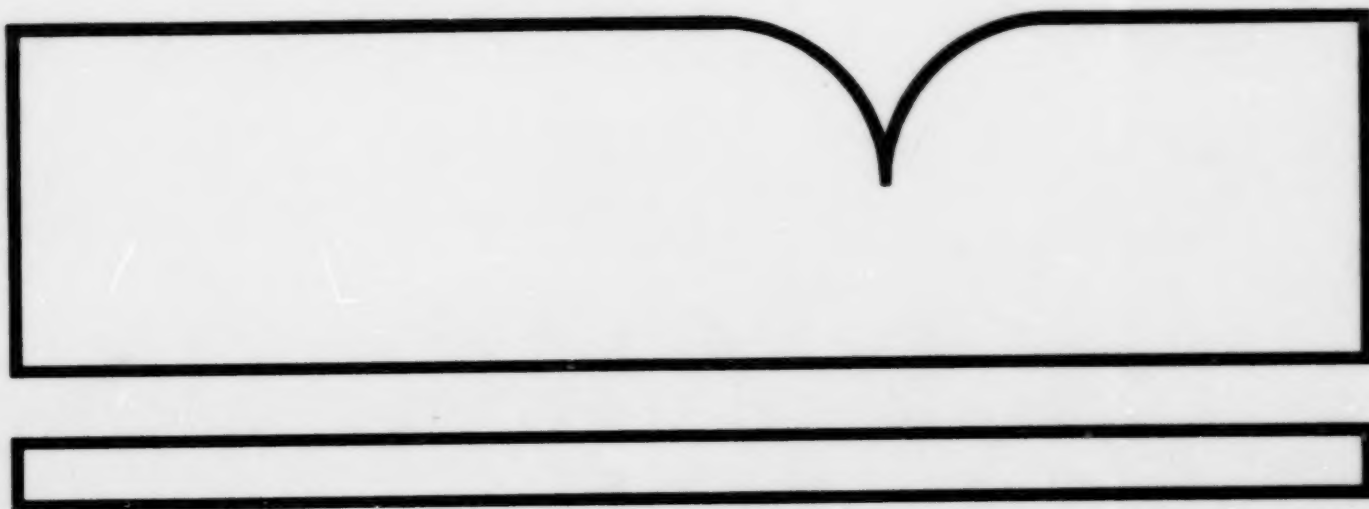
Evaluation and Application of SO_x Measurement
Procedures for Kraft Recovery Furnaces

National Council of the Paper Industry for
Air and Stream Improvement, Inc., New York

Prepared for

Industrial Environmental Research Lab.
Cincinnati, OH

Sep 80



U.S. Department of Commerce
National Technical Information Service

NTIS

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-600/2-80-186	2.	3. RECIPIENT'S ACCESSION NO. PB81 109092
4. TITLE AND SUBTITLE Evaluation and Application of SO _x Measurement Procedures for Kraft Recovery Furnaces		5. REPORT DATE Sept. 1980 Issuing Date.
7. AUTHOR(S) A. K. Jain, R. O. Blosser, D. B. Newport, H. S. Oglesby		6. PERFORMING ORGANIZATION CODE
9. PERFORMING ORGANIZATION NAME AND ADDRESS National Council of the Paper Industry for Air and Stream Improvement, Inc., 260 Madison Avenue, New York, N. Y. 10016		8. PERFORMING ORGANIZATION REPORT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Industrial Environmental Research Laboratory Wood & Food Products Branch Cincinnati, Ohio 45268		10. PROGRAM ELEMENT NO. 1AB604
		11. CONTRACT/GRANT NO. R-804644
		13. TYPE OF REPORT AND PERIOD COVERED Project report 7/76- 9/80
		14. SPONSORING AGENCY CODE EPA/600/12
15. SUPPLEMENTARY NOTES		
16. ABSTRACT The objective of this investigation was to determine the sulfuric acid (SO ₃ /H ₂ SO ₄) and sulfur dioxide (SO ₂) emissions from kraft recovery furnaces using an extractive sampling system. The Goksoyr and Ross controlled condensation technique was chosen. Equipment was designed and fabricated to evaluate the effect of coil length, frit porosity, temperature, flow rate, and concentration upon the efficiency of capture of H ₂ SO ₄ in the modified Graham condenser. The optimum design and operating conditions to minimize SO ₃ /H ₂ SO ₄ losses in filter holders used in the sampling train for particulate separation were determined, and the effects of recovery furnace particulate upon SO ₃ /H ₂ SO ₄ losses were investigated. Sampling of five representative kraft recovery furnace stack gases showed that the SO ₃ /H ₂ SO ₄ concentrations varied from 0 to 2.98 ppm, while the range of SO ₂ concentrations was from 14 to 416 ppm. A comparison of these emissions with the SO ₃ /H ₂ SO ₄ and SO ₂ emissions from oil and coal fired utility boilers shows the kraft recovery furnace emissions to be much lower.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS Kraft Recovery Furnace SO _x Sulfuric Acid Controlled Condensation	b. IDENTIFIERS/OPEN ENDED TERMS Atmospheric	c. COSATI Field/Group .
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

FB81-109092

TOP OF
IMAGE
AREA

EPA-600/2-80-186
September 1980

DROPPED
HEAD
BEGIN
SECTIONS
HERE

EVALUATION AND APPLICATION OF SO₂ MEASUREMENT
PROCEDURES FOR KRAFT RECOVERY^x FURNACES

by

A. K. Jain, R. O. Blosser,
D. B. Newport, H. S. Oglesby
National Council of the Paper Industry
for Air and Stream Improvement, Inc.
New York, New York 10016

Grant No. R804644-01-3

EPA Project Officer:

Michael D. Strutz
Food and Wood Products Division
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

Industrial Environmental Research Laboratory
Office of Research and Development
U. S. Environmental Protection Agency
Cincinnati, Ohio 45268

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

EPA-387 (Cm.)
15-781

PAGE NUMBER

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD;
BEGIN
SECTIONS
HERE

DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory, U. S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U. S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

8 1/2"

9 1/8"

BEGIN
LAST LINE
OF TEXT

3/8"

ii

BOTTOM OF
IMAGE AREA;
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

PAGE NUMBER

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD;
BEGIN
SECTIONS
HERE

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes the laboratory and field studies to measure the sulfur oxides (SO_x) emissions from kraft recovery furnaces. The findings of this report highlight some of the problems associated with using the extractive sampling techniques to measure the SO_x emissions from industrial sources emitting alkaline particulate and describes the techniques used to minimize the errors. When used with appropriate models, the data collected during this investigation may be used to estimate the impact of kraft recovery furnaces upon the ambient SO_x levels. For further information on this subject contact the Food and Wood Products Branch.

David G. Stephan
Director
Industrial Environmental
Research Laboratory
Cincinnati

BEGIN
LAST LINE
OF TEXT

3/8"

iii

BOTTOM OF
IMAGE AREA
(OUTSIDE
DIMENSION
FOR TABLES
AND ILLUS-
TRATIONS)

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD;
BEGIN
SECTIONS
HERE

PREFACE

The increasing recognition of the adverse effects of acid sulfates respiratory systems has resulted in the need for information on sulfuric acid and sulfur dioxide emissions from large industrial sources. One such source is the kraft recovery furnace, readily identified as a possible emitter of acid sulfates because pulping liquor containing large amounts of sulfur compounds is burned in it. This study was the first major laboratory and field effort aimed at determining sulfuric acid emissions from kraft recovery furnaces.

Since the Goksoyr and Ross study in 1962 (J. Inst. Fuel, 35, 177-179, 1962), several investigators have reported on the use of the controlled condensation technique for measuring sulfuric acid emissions from combustion sources. However, very little effort was made to estimate losses during sampling as a result of the interaction of sulfuric acid with any particulate present in the stack gas. The particulates present in flue gases from recovery furnaces are highly alkaline and can easily react with sulfuric acid. Consequently, considerable laboratory effort was made to determine if sulfuric acid losses occurred during sampling and to investigate the techniques of minimizing these losses.

The results reported in this study have not been corrected for any measurement losses sustained in the sampling train because of difficulties encountered in developing a procedure for determining such losses. The data, however, represent the best estimates of sulfuric acid emissions from kraft recovery furnaces using an extractive sampling system.

BEGIN
LAST LINE
OF TEXT

3/8"

iv

BOTTOM OF
IMAGE AREA;
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUS-
TRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD:
BEGIN
SECTIONS
HERE

ABSTRACT

This research program was initiated to determine sulfuric acid ($\text{SO}_3/\text{H}_2\text{SO}_4$) and sulfur dioxide (SO_2) emissions from kraft recovery furnaces using an extractive sampling system.

The Goksoyr and Ross controlled condensation technique, which uses a modified Graham condenser, was chosen because of its reported accuracy. Equipment was designed and fabricated to evaluate the effect of coil length, frit porosity, temperature, flow rate, and concentration on the efficiency of H_2SO_4 capture.

Laboratory tests were also conducted to determine the optimum design and operating conditions to minimize $\text{SO}_3/\text{H}_2\text{SO}_4$ losses in filter holders used in the sampling train for particulate separation. The effects of recovery furnace particulate on $\text{SO}_3/\text{H}_2\text{SO}_4$ losses were investigated. It was observed that the alkaline particulate from the recovery furnace reacted with a part of $\text{SO}_3/\text{H}_2\text{SO}_4$ in the sample. The losses could not be correlated with the alkalinity of the particulate, but based on laboratory investigations, they were less than that required to neutralize the particulate alkalinity.

The equipment was fabricated, and field studies were conducted on five representative kraft recovery furnaces to determine $\text{SO}_3/\text{H}_2\text{SO}_4$ and SO_2 concentrations in flue gases. The $\text{SO}_3/\text{H}_2\text{SO}_4$ concentrations varied from 0 to 2.98 ppm, and the range of SO_2 concentrations was from 14 to 416 ppm. A comparison of these emissions with the $\text{SO}_3/\text{H}_2\text{SO}_4$ and SO_2 emissions from oil-and coal-fired utility boilers shows the kraft recovery furnace emissions to be much lower.

This report was submitted in fulfillment of Grant No. R804644-01-3 by the National Council of the Paper Industry for Air and Stream Improvement under the partial sponsorship of the U. S. Environmental Protection Agency. This report covers a period from July 5, 1976, to July 4, 1979, and work was completed as of May 16, 1979.

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUS-
TRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD:
BEGIN
SECTIONS
HERE

CONTENTS

	Page
Foreword	iii
Preface	iv
Abstract	v
Figures	ix
Tables	x
Abbreviations and Symbols.	xii
Acknowledgments.	xiii
1. Introduction.	1
2. Conclusions	2
3. SO_2 , SO_3 and H_2SO_4 Equilibria in Stack Gas.	3
4. Dewpoint of H_2SO_4	4
5. Methods of SO_2 Measurement in Stack Gas	5
$\text{SO}_3/\text{H}_2\text{SO}_4$ measurement in stack gas	5
SO_2 measurement in stack gas	5
6. Description of Experimental Apparatus and Methods	6
$\text{SO}_3/\text{H}_2\text{SO}_4$ condenser.	6
Sulfuric acid evaporator	6
Laboratory H_2SO_4 sampling train.	10
Methods of H_2SO_4 analysis in liquid solutions.	10
Determination of H_2SO_4 capture efficiency of Greenburg-Smith impingers	10
Filter holder design and particulate interference determinations.	10
Determination of $\text{SO}_3/\text{H}_2\text{SO}_4$ condenser efficiency	13
Determination of H_2SO_4 losses in filter holders	13
Determination of SO_2 capture efficiency of Greenburg-Smith impingers	17
7. Results of Laboratory Studies	19
Methods of sulfate analysis.	19
H_2SO_4 capture efficiencies of Greenburg- Smith impingers.	20
Efficiency of SO_3 condensation coil.	20
Loss of H_2SO_4 in filter holders.	22
SO_2 capture efficiency of Greenburg- Smith impingers.	27

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUS-
TRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD,
BEGIN
SECTIONS
HERE

Page

	Tests with electrostatic precipitator filter in $\text{SO}_3/\text{H}_2\text{SO}_4$ sampling train	28
8.	Field Measurements of SO_x Emissions.	31
	Sources sampled	31
	SO_x sampling train with quartz filter	32
	SO_x sampling train with electrostatic precipitator.	34
	Test procedure.	34
	SO_x emission data	35
	Discussion.	38
	References	43
	Appendices	
	A. Methods of sulfate analysis	45
	B. Calculations.	47
	C. H_2SO_4 losses in blank runs with quartz filter and filter holder in line.	50

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD;
BEGIN
SECTIONS
HERE

FIGURES

<u>Number</u>		<u>Page</u>
1	H ₂ SO ₄ condenser	7
2	H ₂ SO ₄ evaporation assembly.	8
3	Modified H ₂ SO ₄ evaporation assembly	9
4	H ₂ SO ₄ sampling train.	11
5	Quartz filter holder.	12
6	Condenser efficiency determination equipment--flow diagram	14
7	Filter loss determination equipment-- flow diagram.	15
8	Quartz filter loss determination equipment--flow diagram	16
9	Schematic for determining H ₂ SO ₄ losses with continuous loading of particulate.	18
10	Electrostatic precipitator.	29
11	SO _x sampling train.	33
12	SO ₃ measurement field data sheet.	36

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD;
BEGIN
SECTIONS
HERE

TABLES

<u>Number</u>		<u>Page</u>
1	Sodium Interference with Thorin Titration.	20
2	H ₂ SO ₄ Capture Efficiency of Greenburg-Smith Impingers.	21
3	Effect of Frit Porosity Upon SO ₃ Condenser Efficiency	21
4	Effect of Flow Rate on Capture Efficiency of SO ₃ Condenser.	22
5	Effect of H ₂ SO ₄ Concentration on Capture Efficiency	23
6	Effect of Quartz Filter Assembly Upon Sample Recovery.	24
7	Filter Holder Losses for Different Particulate Samples.	24
8	Results of Blank Runs Through Quartz Filter Holder.	25
9	H ₂ SO ₄ Losses in Tests with Na ₂ SO ₄	26
10	H ₂ SO ₄ Losses in Tests with Na ₂ CO ₃ and Na ₂ CO ₃ + Na ₂ SO ₄	26
11	H ₂ SO ₄ Losses in Tests with Recovery Particulate.	27
12	SO ₂ Capture Efficiency of Greenburg-Smith Impingers.	28
13	Oxidation of SO ₂ to SO ₃ in Electrostatic Precipitator	30
14	Recovery Furnace A SO _x Data.	37
15	Recovery Furnace B SO _x Data.	37
16	Recovery Furnace C SO _x Data.	38
17	Recovery Furnace D SO _x Data.	39
18	Recovery Furnace E SO _x Data.	39
19	SO ₃ /H ₂ SO ₄ Emission Data Summary.	40
20	Coefficient of Correlation Between SO ₃ /H ₂ SO ₄ and SO ₂	41
21	SO _x Emissions from Oil- and Coal-Fired Utility and Industrial Boilers	42

BEGIN
LAST LINE
OF TEXT

3/8"

x

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD
BEGIN
SECTIONS
HERE

ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

cm	-- centimeter
g	-- grams
l/mole	-- liters/mole
lpm	-- liters per minute
ml	-- milliliter
mm	-- millimeter
ppm	-- parts per million
g/dscm	-- grams/dry standard cubic meter
gr/dscf	-- grains/dry standard cubic foot

SYMBOLS

H ₂ O	-- water
H ₂ SO ₄	-- sulfuric acid
O ₂	-- oxygen
SO ₂	-- sulfur dioxide
SO ₃	
	-- sulfur trioxide
SO _x	-- sulfur oxides
K	Equilibrium constant
P _{H₂O}	Partial pressure of H ₂ O
P _{H₂SO₄}	Partial pressure of H ₂ SO ₄
T	Temperature
r	Coefficient of correlation

BEGIN
LAST LINE
OF TEXT

3/8"

xi

PAGE NUMBER

BOTTOM
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLE
AND ILLUSTRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD
BEGIN
SECTIONS
HERE

ACKNOWLEDGMENTS

The cooperation of five kraft mills where the field tests were conducted is gratefully acknowledged. They provided the sampling locations and assisted us in conducting the tests.

D. Bruce Harris of the U. S. EPA, Industrial Environmental Research Laboratory, and Kenneth Cushing of Southern Research Institute provided the first electrostatic precipitator and assisted in our attempt to apply this technique. James E. Cheney of the U. S. EPA, Industrial Environmental Research Laboratory, loaned us the electrostatic precipitator that was finally used in our study. His guidance and assistance was invaluable.

John Ruppertsberger was the first project officer and continued his interest in the project even after his responsibilities ended. Michael Strutz was assigned as the new project officer.

BEGIN
LAST LINE
OF TEXT

3/8"

xii

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUS-
TRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD,
BEGIN
SECTIONS
HERE

SECTION 1

INTRODUCTION

The presence of acid sulfate aerosols in the ambient air is of special concern in air quality management programs because of their known adverse effect on respiratory functions. One of the precursors of ambient acid sulfate aerosols is sulfur trioxide (SO_3), which is formed during the combustion of sulfur containing fossil fuels.

In the kraft pulping industry the concentrated spent cooking liquor (black liquor), which consists of wood components, inorganic chemicals, and sulfur compounds, is sprayed into a furnace and combusted. Although in a kraft recovery furnace black liquor is burned in a manner to minimize sulfur dioxide (SO_2) generation, the presence of high concentrations of sulfur in the black liquor has raised the question of the possible presence of (SO_3)/sulfuric acid (H_2SO_4) in kraft recovery furnace flue gas.

The objective of this investigation was to determine representative SO_2 and $\text{SO}_3/\text{H}_2\text{SO}_4$ levels in kraft recovery furnace emissions. The investigation was divided into the following areas:

- (1) Development and laboratory testing of a suitable method to measure $\text{SO}_3/\text{H}_2\text{SO}_4$ concentration in a particulate-free gas stream,
- (2) Determination of the effect of the presence of kraft recovery furnace particulate on the measurement of $\text{SO}_3/\text{H}_2\text{SO}_4$,
- (3) Selection and testing of a suitable particulate separation device to minimize particulate interaction with $\text{SO}_3/\text{H}_2\text{SO}_4$ in the sampling train if particulate is found to interfere in $\text{SO}_3/\text{H}_2\text{SO}_4$ measurement, and
- (4) Measurement of SO_2 and $\text{SO}_3/\text{H}_2\text{SO}_4$ levels in kraft recovery furnaces from five representative sources in the southeast.

The intensive laboratory and field investigation carried out in this program, consistent with current technology, provides the best estimates of SO_2 and $\text{SO}_3/\text{H}_2\text{SO}_4$ emissions from five representative kraft recovery furnaces.

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD
BEGIN
SECTIONS
HERE

SECTION 2

CONCLUSIONS

Extensive laboratory studies were carried out to develop and evaluate a method for measuring $\text{SO}_3/\text{H}_2\text{SO}_4$ in kraft recovery furnaces. Field tests utilizing the controlled condensation technique were conducted to determine the emissions of SO_2 and $\text{SO}_3/\text{H}_2\text{SO}_4$ from several representative sources. The following observations were made:

- (1) Thorin titration was found acceptable for sulfate analysis. However, interference studies showed that sodium ions caused a positive interference.
- (2) The efficiency of H_2SO_4 capture in SO_3 condensers was found to be dependent upon the frit porosity and coil length. Best results were obtained with Ace Glass Type C frit and a 200-cm coil when the temperature was maintained at 75 to 85°C (167 to 195°F).
- (3) The flow rate and concentration of H_2SO_4 did not significantly affect the efficiency of H_2SO_4 capture in the condenser over the flow and concentration conditions studied.
- (4) The quartz filter assembly did not cause any loss of H_2SO_4 when it was maintained above 260°C (500°F).
- (5) In the presence of particulate, H_2SO_4 losses across the filter holder varied for different particulate samples.
- (6) Field tests on five kraft recovery furnaces showed $\text{SO}_3/\text{H}_2\text{SO}_4$ concentrations on the order of 0 to 2.98 ppm, with an average of 0.81 ppm. The SO_2 concentrations during these tests varied from 14 to 416 ppm.
- (7) An analysis of the emission data showed a poor correlation between $\text{SO}_3/\text{H}_2\text{SO}_4$ and SO_2 concentrations.

BEGIN
LAST LINE
OF TEXT

3/8"

WIDTH OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

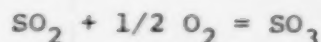
TOP OF
IMAGE
AREA

DROPPED
HEAD
BEGIN
SECTION
HERE

SECTION 3

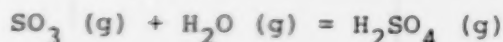
SO_2 , SO_3 , AND H_2SO_4 EQUILIBRIA IN STACK GAS

When fuels containing sulfur are burned in a furnace, a fraction of SO_2 formed during combustion is oxidized to SO_3 according to the following reaction:



The formation of SO_3 is not favored above 540°C (1000°F), and even at lower temperatures, the kinetics of the above reaction are unfavorable in the absence of catalysts. Consequently, SO_3 levels generally lower than those predicted by assuming thermodynamic equilibrium are observed in stack gases.

SO_3 is a very strong acid and reacts with water (H_2O) vapors present in the stack gas to form sulfuric acid:



The equilibrium constant, K , for the above reaction is given by:

$$K = \frac{(\text{H}_2\text{SO}_4)}{(\text{H}_2\text{O}) (\text{SO}_3)} \quad 1/\text{mole}$$

In the temperature range 325°C (617°F) to 483°C (901°F), K may be estimated by the following equation (1, 2, 3):

$$\log (1/K) = \frac{22850}{4.571T} + 0.75 \log T - 0.00057T + 4.086$$

where temperature, T , is defined in $^\circ\text{K}$.

If the above equation is used to predict the fraction of SO_3 that would be present as H_2SO_4 in kraft recovery furnace stack gases, which are typically at 150 to 210°C (302 to 410°F) and contain 20 to 30 volume percent moisture, it can be stated that all the SO_3 present in a kraft recovery furnace stack gas would essentially exist as H_2SO_4 .

BEGIN
LAST LINE
OF TEXT

1/8"

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD
BEGIN
SECTIONS
HERE

SECTION 4

DEWPOINT OF H_2SO_4

Since Thomas and Barker (4), many workers have investigated the dewpoint of sulfuric acid. However, the historical data on the dewpoint of dilute mixtures of SO_3 and H_2SO_4 vary considerably.

Abel (5) published the first report to use thermodynamic data to calculate partial pressures of H_2SO_4 , SO_3 , and H_2O . Combining Abel's data with Greenwalt's (6) H_2O partial pressures over H_2SO_4 solutions, H_2SO_4 - H_2O dewpoint charts were prepared (1, 5, 6). These charts can be used to predict dewpoint temperature for a gas containing known concentrations of H_2SO_4 and H_2O vapor.

In addition to calculation procedures based upon thermodynamic data, many investigators used a number of techniques to determine dewpoints of gases containing H_2SO_4 and H_2O vapors. Of all the methods used, the most reliable method of measuring H_2SO_4 dewpoint is the experimental condensation method used by Lisle and Sensenbaugh (7) and others (3, 8). Lisle and Sensenbaugh's data correlate very well with Muller's calculated dewpoints. Martin (8) used laboratory data obtained by using controlled condensation techniques to generate a set of curves for $\text{SO}_3/\text{H}_2\text{SO}_4$ concentration below 100 ppm.

An empirical equation that predicts the dewpoint temperature for known concentration of H_2SO_4 and H_2O vapors was developed by Verhoff and Banchemo (9). According to them the dewpoint may be estimated by the following equation:

$$1000/T = 2.276 - 0.02943 \ln p_{\text{H}_2\text{O}} - 0.0858 \ln p_{\text{H}_2\text{SO}_4} \\ + 0.00620 (\ln p_{\text{H}_2\text{SO}_4}) (\ln p_{\text{H}_2\text{O}})$$

where 'T' is the dewpoint in °K, and $p_{\text{H}_2\text{O}}$ and $p_{\text{H}_2\text{SO}_4}$ are the partial pressures of H_2O and H_2SO_4 , respectively, in mm Hg.

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD:
BEGIN
SECTIONS
HERE

SECTION 5

METHODS OF SO_x MEASUREMENT IN STACK GAS

$\text{SO}_3/\text{H}_2\text{SO}_4$ MEASUREMENT IN STACK GAS

Several methods, including selective condensation, absorption in isopropyl alcohol, and electrical conductivity measurement, have been used in the determination of $\text{SO}_3/\text{H}_2\text{SO}_4$ concentrations and dewpoints in stack gases. However, the simplest and most reproducible method of measuring H_2SO_4 in a stack gas is the selective condensation method developed by Goksoyr and Ross (3, 7, 10, 11). Consequently, the condensation method was used in this investigation.

In the selective condensation method, the flue gas after separation of particulates is passed through a condensation coil where it is cooled to below 85°C (185°F) but maintained above the dewpoint of water vapor present. The sulfuric acid condenses in the coil and is recovered by washing the coil with isopropyl alcohol. Since no water vapor is condensed, SO_2 is not retained with the sulfuric acid.

SO_2 MEASUREMENT IN STACK GAS

The method of SO_2 measurement in the stack gas was essentially the same as EPA Method 6 (14). The procedure involves passing the sample through two midget impingers in series, each containing 3 percent hydrogen peroxide, at a rate of 1 lpm for 20 minutes. The impinger content is titrated with barium perchlorate with Thorin indicator. During this investigation the flue gas SO_2 concentration was measured after the $\text{SO}_3/\text{H}_2\text{SO}_4$ had been removed from the sample gas by the condensation coil. Additionally, since higher sample flow rates were required during sampling, the midget impingers were replaced with two Greenburg-Smith impingers, each containing 100 ml of 3 percent hydrogen peroxide.

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

SECTION 6

DESCRIPTION OF EXPERIMENTAL APPARATUS AND METHODS

$\text{SO}_3/\text{H}_2\text{SO}_4$ CONDENSER

Several types of different equipment were fabricated and tested in the laboratory to assess the effect of variables that influence $\text{SO}_3/\text{H}_2\text{SO}_4$ measurement in stack gases. The modified Graham condenser used for capturing $\text{SO}_3/\text{H}_2\text{SO}_4$ is shown in Figure 1. The inside diameter of the glass tubing for the condenser coil was 5 mm, and the frit diameter was 45 mm. Three different condensers were evaluated. In the first condenser, approximately 90 cm of glass tubing was used to make the condenser coil, and a coarse glass frit (Ace Glass Type B) was used. The second condenser contained 140 cm of glass tubing and an Ace Glass Type D frit. The third condenser had 180 cm of glass tubing and an Ace Glass Type C frit. During the tests each condenser was filled with water and its temperature was maintained at 75 to 85°C (167 to 185°F) with a heating mantle. Thermocouples were used to measure the condenser temperature as well as the temperature of the gas stream leaving the condenser.

SULFURIC ACID EVAPORATOR

A sulfuric acid evaporator (Figure 2) was used in the laboratory to generate test gases containing desired concentrations of moisture and H_2SO_4 . The evaporator was fabricated with a 15-mm O.D. quartz tube packed with glass beads and wrapped with a heating element and insulation. A coarse quartz frit was installed inside the evaporator tube to eliminate slugging and provide uniform H_2SO_4 concentration during a test. Very dilute sulfuric acid was added to the evaporator in the middle of the heated zone with a low flow rate variable speed pump (Masterflex, Cole Parmer, Chicago, Illinois). The concentration of H_2SO_4 and moisture in the gas stream was varied by changing the normality of H_2SO_4 solution and its rate of addition to the evaporator. The temperature of the evaporator was maintained above 320°C (608°F).

A modified sulfuric acid evaporator was used in later studies (Figure 3) to minimize the problem of uneven flow or slugging, observed with the first evaporator. The equipment consisted of a nebulizer (Aerosol Generator Assembly, #7002, Civitron KDC, Inc., Anaheim, California), an evaporation chamber maintained above 230°C (446°F), and a conditioning tube maintained

BEGIN
FIRST
LINE OF
TEXT
HERE

CHOPPED
PAD
BE IN
SECTIONS
HERE

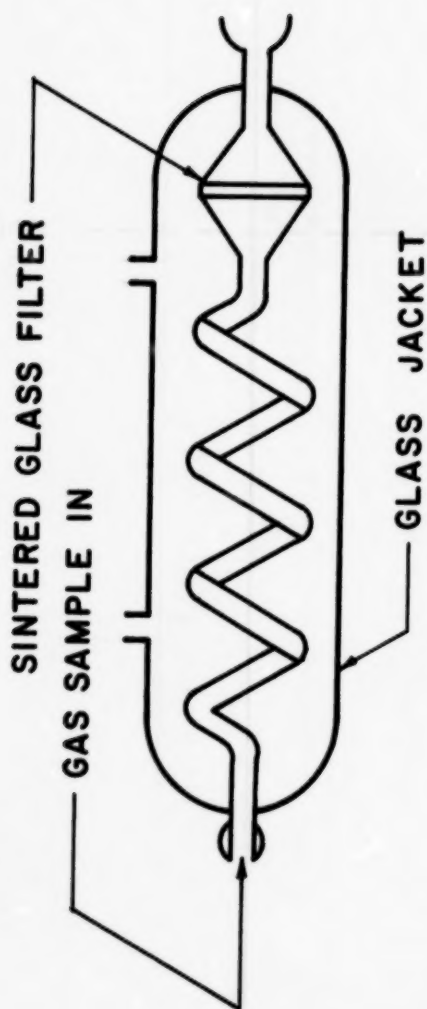


Figure 1. H_2SO_4 condenser.

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
EXTEND
DIMENSION
FOR TABLE
AND ILLUSTRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

DROPPED
HEAD
BEGIN
SECTIONS
HERE

TOP OF
IMAGE
AREA

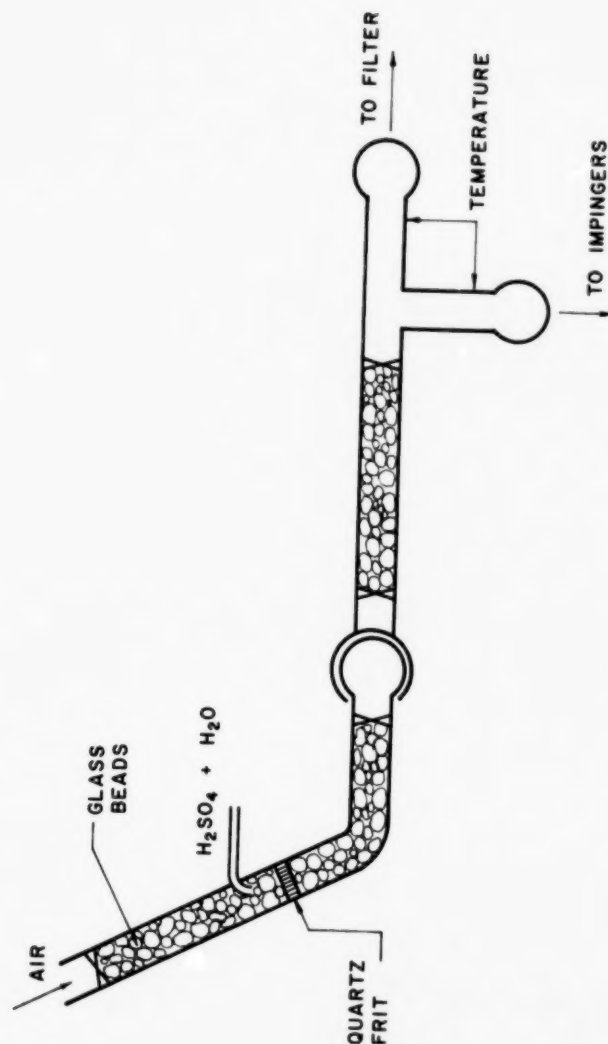


Figure 2. H_2SO_4 evaporation assembly.

BEGIN
LAST LINE
OF TEXT

RIGHT OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TAIL
AND ILLU
STRATIONS

RIGHT
FIRST
LINE OF
TEXT
HERE

DISPLAYED
HEAD
SECTION
HERE

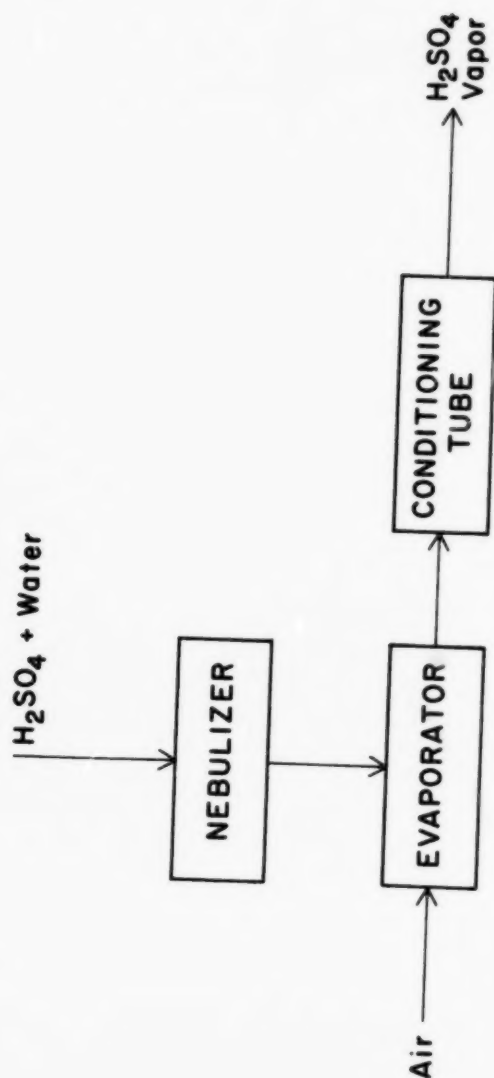


Figure 3. Modified H_2SO_4 evaporation assembly.

RIGHT
LAST LINE
OF TEXT

BOTTOM OF
PAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

above 340°C (644°F). The concentration of H_2SO_4 in the gas stream was adjusted by changing the normality of H_2SO_4 solution to the nebulizer. Compressed air was used to run the nebulizer. Although the use of a nebulizer provided very little flexibility in changing the moisture content of the gas stream, a stable and uniform H_2SO_4 concentration was obtained.

LABORATORY H_2SO_4 SAMPLING TRAIN

The laboratory sampling train for determining sulfuric acid concentration in the gas stream leaving the condenser (Figure 4) consisted of two Greenburg-Smith impingers containing isopropyl alcohol, an impinger containing deionized water, a column of silica gel, a leakfree vacuum pump, a rotameter, and a calibrated dry gas meter. The impingers were kept in an ice bath.

METHODS OF H_2SO_4 ANALYSIS IN LIQUID SOLUTIONS

Two methods of sulfate analysis were investigated to determine their precision and ease of use. The first used dimethylsulfonazo III as the indicator and standard barium perchlorate as the titrant. The second used Thorin as the indicator and barium perchlorate as the titrant. Interference of sodium ions in Thorin titration was also investigated. The details of the analytical procedure are described in Appendix A.

DETERMINATION OF H_2SO_4 CAPTURE EFFICIENCY OF GREENBURG-SMITH IMPINGERS

The sampling train to determine the H_2SO_4 capture efficiency of Greenburg-Smith impingers consisted of four impingers. The first three contained 100 ml of 90% isopropyl alcohol each and the fourth impinger contained 100 ml of deionized water. The gases leaving the last impinger passed through a column of silica gel, a vacuum pump, a rotameter, and a dry gas meter. Tests were conducted by passing gas streams containing H_2SO_4 vapors through the impingers for 30 minutes. The contents of the impingers were then analyzed for H_2SO_4 . The effects of H_2SO_4 concentration and gas flow rate through the impingers were studied.

FILTER HOLDER DESIGN AND PARTICULATE INTERFERENCE DETERMINATIONS

Initially filter holders typically used in EPA Method 5 (12) sampling trains were used. These filter holders are not designed for use above 205°C (400°F) and failed when their temperature was raised much above 233°C (450°F). Since sulfuric acid was found on filter holders maintained below 260°C (500°F), a quartz filter holder (Figure 5) was used. The details of the design are specified elsewhere (11). The filter medium used in all the tests was Tissuequartz 2500 QAO (Pallflex Products Corporation, Putnam, Connecticut).

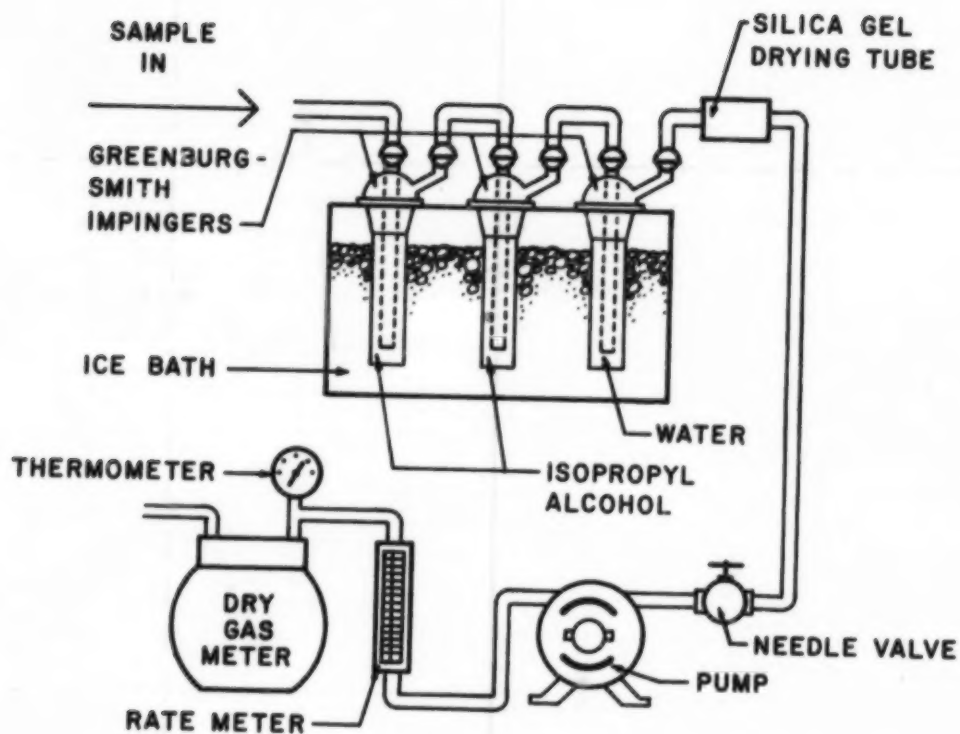


Figure 4. H_2SO_4 sampling train.

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD:
BEGIN
SECTIONS
HERE

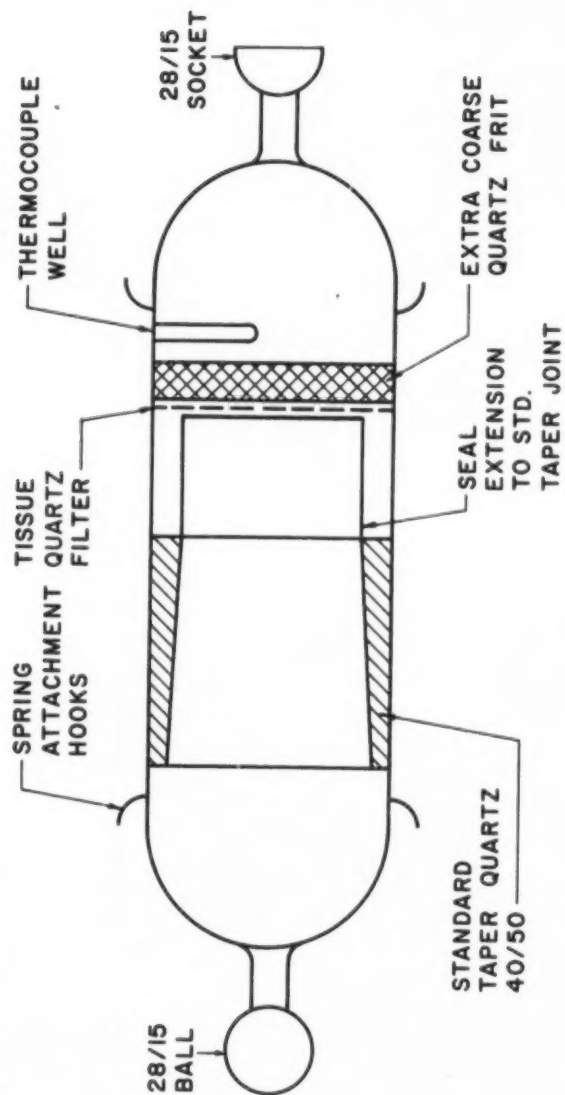


Figure 5. Quartz filter holder.

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA.
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUS-
TRATIONS

During the first phase of the study, in order to determine the effects of recovery furnace particulate upon H_2SO_4 losses, the filters were preloaded with measured amounts of particulate by slowly adding particulate directly to the filters while drawing air through them at a high rate. Gas samples containing H_2SO_4 vapors were then passed through the filters. In subsequent tests the equipment was modified to enable continuous loading of the filter with particulate while passing H_2SO_4 through it.

DETERMINATION OF SO_3/H_2SO_4 CONDENSER EFFICIENCY

Figure 6 shows the schematic of the sampling system used for determining the efficiencies of H_2SO_4 capture in the modified Graham condensers. Tests were conducted at different flow rates through the condensers and with various H_2SO_4 concentrations in the gas stream. Each test lasted approximately 30 minutes. At the end of each test the condenser was washed and analyzed for sulfuric acid that was retained in the condenser. The impinger contents were also analyzed to determine the amount of H_2SO_4 passing through the condenser.

DETERMINATION OF H_2SO_4 LOSSES IN FILTER HOLDERS

EPA Method 5 Filter Holders

The initial tests to determine the condensation of H_2SO_4 vapors in the filter holder were conducted at 175 to 200°C, and filter holders used in EPA Method 5 (12) sampling trains were used (Figure 7). Gas streams containing H_2SO_4 vapors were passed through these filter holders at different flow rates for approximately 30 minutes. At the end of 30 minutes the filters were disconnected, allowed to cool down, and washed with isopropyl alcohol to determine the amount of H_2SO_4 retained on the filter holder. The impinger contents were also analyzed to determine the amount of H_2SO_4 passing through the filter holders.

Quartz Filter Holders

Tests with EPA Method 5 filter holders showed that they retained significant amounts of H_2SO_4 when maintained below 200°C. However, when the temperature of these filter holders was raised above 200°C, the gasket materials used in these filter holders failed. Consequently, quartz filter holders were tested in the laboratory.

The initial tests with quartz filter holders used the schematic shown in Figure 8. Gas streams containing H_2SO_4 were passed through filter holders maintained above 260°C to determine H_2SO_4 losses when (a) there was no particulate filter holder in the sample train, (b) there was a quartz filter holder in the sample train, and (c) the quartz filter holder was preloaded with particulate samples from different recovery furnaces. The

BEGIN
BUILD
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
ON PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD
BEGIN
SECTION
LINE

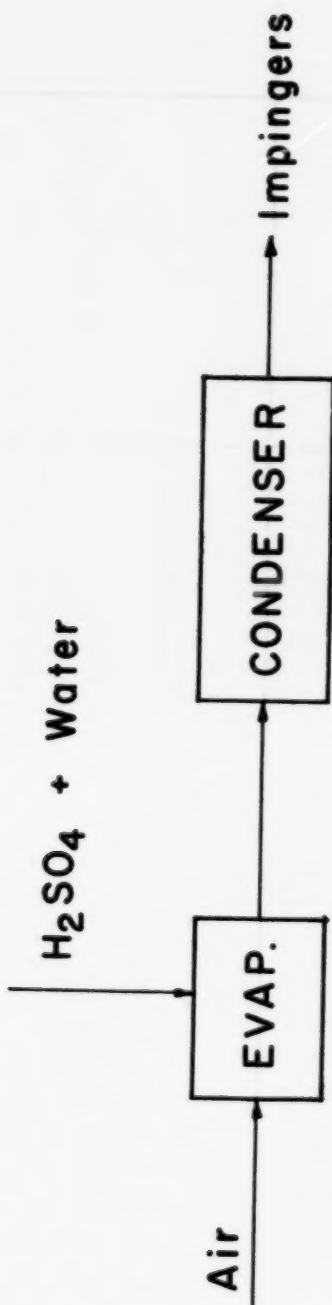


Figure 6. Condenser efficiency determination equipment--flow diagram.

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD
BEGIN
SECTIONS
HERE

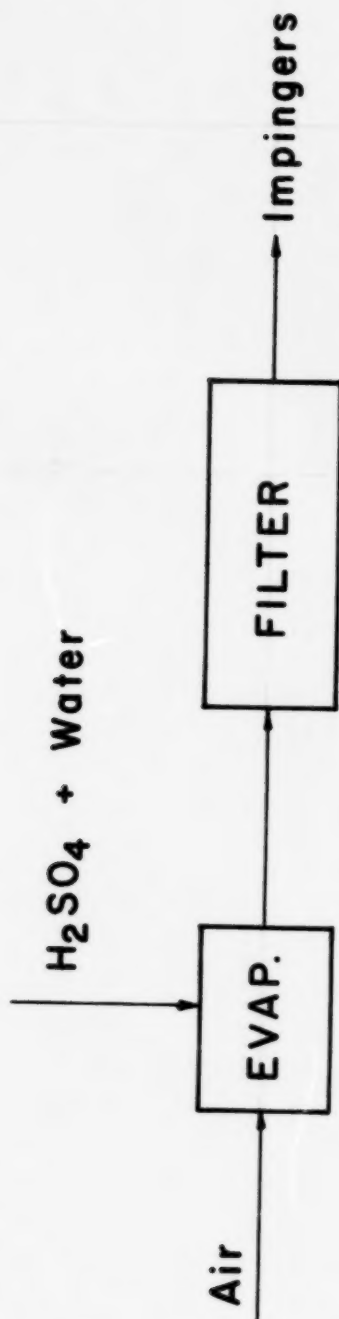


Figure 7. Filter loss determination equipment--flow diagram.

BEGIN
LAST LINE
OF TEXT

5/8"

BOTTOM OF
IMAGE AREA
EXTRUSION
FOR TABLES
AND ILLUSTRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

1.5 INCH
OR MORE

TOP OF
PAGE
AREA

DROPPED
HEAD
BEGIN
SECTION
HERE

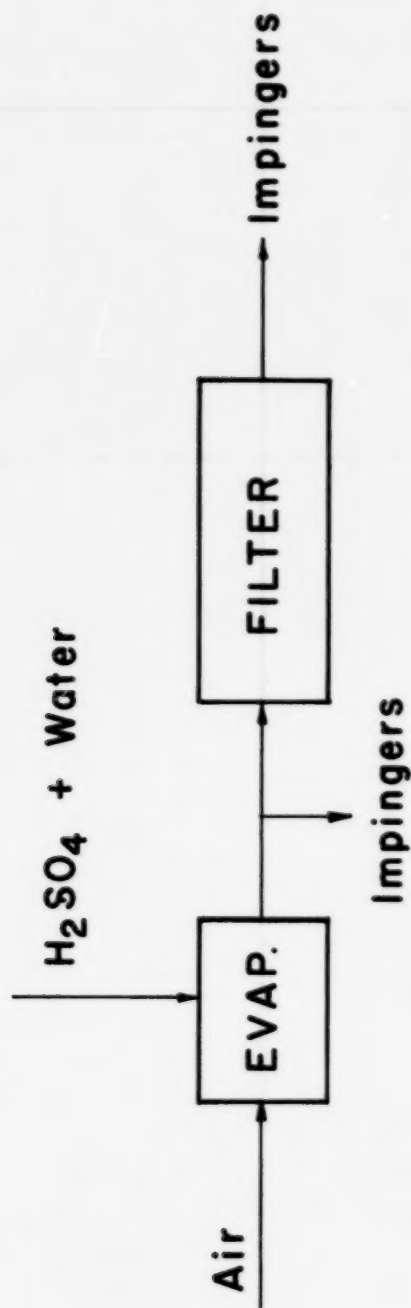


Figure 8. Quartz filter loss determination equipment--flow diagram.

BEGIN
LAST LINE
OF TEXT

1 INCH

16

PAGE NUMBER

BOTTOM OF
PAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND FIGURE
CAPTIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

amount of preloaded particulate on the filter paper in each test was equivalent to a 30-minute sampling run at 8 lpm and an average particulate concentration of approximately 0.2 g/dscm (0.088 gr/dscf).

DROPPED
HEAD
BEGIN
SECTION
HERE

The equipment used to determine H_2SO_4 losses when the quartz filters were continuously loaded with particulate while the H_2SO_4 vapor was being passed through them, thus simulating stack conditions, is shown in Figure 9. H_2SO_4 aerosol was generated in the nebulizer (N1), passed through evaporation chamber E1 ($\sim 200^\circ C$ at T1) and the conditioning and sampling tube ($\sim 260^\circ C$ at T2), and entered the mixing tube. Evaporator E2 was connected to the mixing tube and heated to maintain the conditioning tube temperature at $260^\circ C$. If particulate was to be added to the filter, nebulizer N2 was used to generate aerosols from salt cake solution, which were passed through evaporator E2 to generate particulate. The streams containing particulate and H_2SO_4 were mixed in the mixing chamber and passed through the particulate filter, which was maintained at $285^\circ C$. Tests were conducted to determine H_2SO_4 losses for several particulate samples at different H_2SO_4 concentrations.

DETERMINATION OF SO_2 CAPTURE EFFICIENCY OF GREENBURG-SMITH IMPINGERS

Three Greenburg-Smith impingers, each containing 100 ml of 3 percent hydrogen peroxide, were used to determine their SO_2 capture efficiency. The gases leaving the last impinger passed through a column of silica gel, a vacuum pump, a rotameter, and a dry gas meter. Tests were conducted by passing gas streams containing different concentrations of SO_2 through the impingers for 30 minutes. The contents of the first and second impinger were combined and analyzed for H_2SO_4 . The third impinger solution was separately analyzed for H_2SO_4 .

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

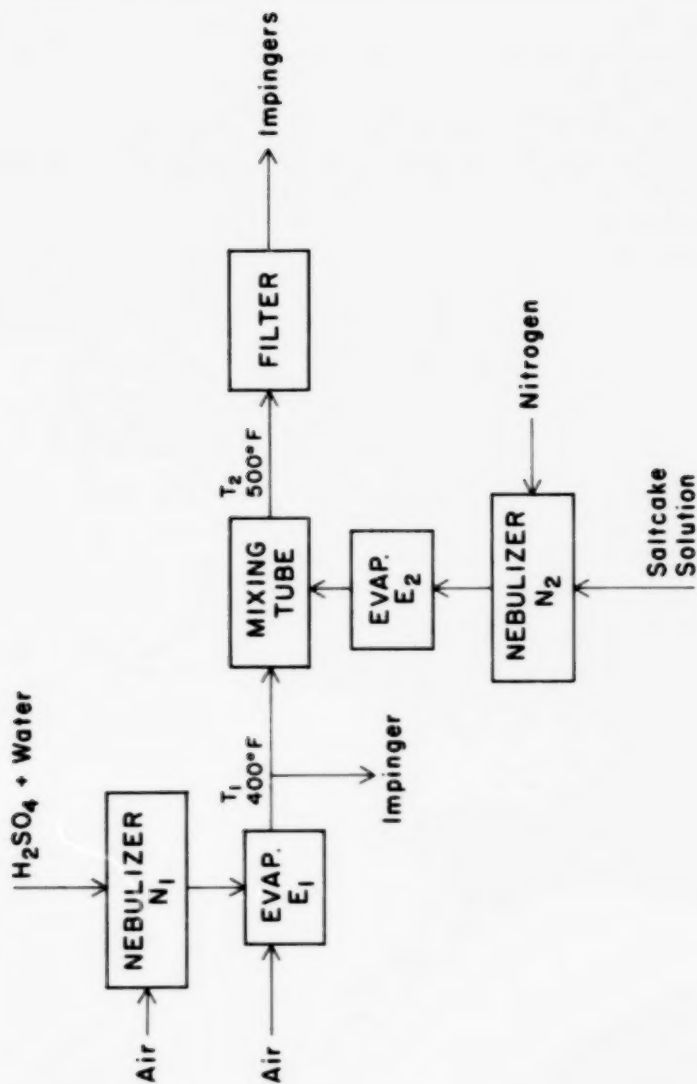


Figure 9. Schematic for determining H_2SO_4 losses with continuous loading of particulate.

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD,
BEGIN
SECTIONS
HERE

SECTION 7

RESULTS OF LABORATORY STUDIES

METHODS OF SULFATE ANALYSIS

Sulfate Determination with Dimethylsulfonazo III Indicator

The initial tests for sulfate, which utilized dimethylsulfonazo III as indicator, were promising. However, problems were encountered later, and it was felt that the change in color at the end point was so subtle that its identification would be difficult. As a result, this method was not used.

Sulfate Determination with Thorin Indicator

Problems of failure to observe the end point accurately were noted during initial tests in which Thorin was used as the indicator. It was determined that these problems were encountered either when there was less than 80 percent isopropyl alcohol in the solution to be titrate or when too much titrant was required during titration.

These problems were corrected by (a) adding adequate amounts of isopropyl alcohol to the sample and (b) analyzing small enough samples that required no more than 10 ml of 0.003 N barium perchlorate during titration. After these changes were made in the laboratory procedure, Thorin titration was found to be very accurate and reproducible.

Since sodium constitutes a large fraction of recovery furnace particulates, tests were conducted to determine sodium ion interference with Thorin titration. The results (Table 1) show that when no sodium was present in the sample, the volume of titrant required to titrate 10.0 ml of sample was 9.1 ml. However, when different amounts of sodium nitrate solution were added to a 10-ml sample and the mixture was analyzed, the volume of titrant required increased with increase in volume of added sodium nitrate. Since nitrate is not an interference in sulfate titration, these results indicate that sodium ions caused a positive interference in sulfate analysis when Thorin indicator was used.

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

BEGIN
LAST LINE
OF TEXT

TABLE 1. SODIUM INTERFERENCE WITH THORIN TITRATION

No.	Vol. 0.01 N NaNO ₃ (ml)	Vol. 0.022 N Ba(ClO ₄) ₂ Titrant (ml)
1	0	9.10
2	10	9.15
3	20	9.30
4	30	9.45
5	40	9.65

H₂SO₄ CAPTURE EFFICIENCIES OF GREENBURG-SMITH IMPINGERS

The results of the tests to determine H₂SO₄ capture efficiencies of Greenburg-Smith impingers are recorded in Table 2. For nine runs, an average 97.5 percent of a known amount of the acid was captured in the first impinger, and the remaining was captured in the second impinger. No acid was found in the third impinger for the entire range of gas flow rates and acid concentrations. Based upon these results, only two Greenburg-Smith impingers in series were used to capture H₂SO₄ from sample streams in subsequent laboratory tests.

EFFICIENCY OF SO₃ CONDENSATION COIL

Effect of Frit Porosity and Coil Length on Condenser Efficiency

The results of the tests aimed at determining the effect of frit porosity upon the efficiency of SO₃ condensation are recorded in Table 3. During these tests the temperature of the condenser was maintained between 75 and 85°C (167 and 185°F). The low efficiency of H₂SO₄ capture with the Type B frit may be due partially to the smaller length of the condensing coil. Type D frit gave very high capture efficiency, but did not allow sample flow rates greater than 2 lpm. Frit Type C was found to be most acceptable from the point of view of sample flow rate and efficiency of H₂SO₄ capture.

Effect of Flow Rate on Condenser Capture Efficiency

The results of tests aimed at determining the effect of flow rate on the efficiency of SO₃ condensation are summarized in

BEGIN
 FIRST
 LINE OF
 TEXT
 HERE

TYPING GUIDE SHEET

CENTER
 OF PAGE

TOP OF
 IMAGE
 AREA

TABLE 2. H_2SO_4 CAPTURE EFFICIENCY OF GREENBURG-SMITH IMPINGERS

Run No.	H_2SO_4 Conc., ppm	Flow Rate, lpm	Percent Capture		
			1st Impinger	2nd Impinger	3rd Impinger
1	0.6	6.0	100.0	0	0
2	1.2	7.6	93.4	6.6	0
3	7.7	7.7	97.8	2.2	0
4	78.0	5.8	100.0	0	0
5	78.0	4.7	97.5	2.5	0
6	65.2	2.9	95.4	4.6	0
7	6.6	1.7	96.1	3.9	0
8	10.0	1.5	97.1	2.9	0
9	59.0	1.8	100.0	0	0
Mean			97.5	2.5	

TABLE 3. EFFECT OF FRIT POROSITY UPON SO_3 CONDENSER EFFICIENCY

No.	Frit Type*	Max. Pore Dia. Range (μm)	Length of Condensing Coil, (cm)	Flow Rate (lpm)	% H_2SO_4 Capture
1	B	70-100	100	2	20-40
2	D	10-20	200	2	99
3	C	25-50	200	2-8	90-99

BEGIN
 LAST LINE
 OF TEXT

BOTTOM OF
 IMAGE AREA;
 OUTSIDE
 DIMENSION
 FOR TABLES
 AND ILLUS-
 TRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

Typing Guide Sheet

CENTER
ON PAGE

TOP OF
IMAGE
AREA

Table 4. The results show that the efficiency of H_2SO_4 capture varied from 90.0 to 99.4 percent during these tests and was slightly higher during the high flow rate tests.

CROPPED
HEAD
BELOW
SECTION
HERE

Effect of H_2SO_4 Concentration on Condenser Capture Efficiency

Tests were conducted in the concentration range of 1 to 50 ppm to determine if there was any effect of H_2SO_4 concentration on its percent of capture. The results are summarized in Table 5. All the tests were made at a flow rate of approximately 9 lpm. The results show that the efficiencies of capture were generally higher than 95 percent, except when 50 ppm H_2SO_4 was present in the gas stream. However, only two runs were made at high H_2SO_4 concentration.

When a t test was performed to test the hypothesis that the mean efficiencies of capture were different for 1 and 50 ppm H_2SO_4 samples, it was concluded that there was insufficient evidence to indicate that the two efficiencies of capture were different at the 0.05 level of significance.

LOSS OF H_2SO_4 IN FILTER HOLDERS

EPA Method 5 Type Filter Holders

Tests with EPA Method 5 type of filter holders were conducted by maintaining the filter holders in the temperature range of 175 to 200°C. The results of six tests showed that on an average 45 percent of the H_2SO_4 present in the gas stream was retained in the filter holder. These results indicated the need to maintain the filter holder at higher temperatures, which was not possible with these type filter holders.

TABLE 4. EFFECT OF FLOW RATE ON
CAPTURE EFFICIENCY OF SO_3 CONDENSER

Flow Rate (lpm)	No. of Runs	% H_2SO_4 Capture		
		Max.	Min.	Avg.
3.5	7	96.8	90.0	93.3
9.5	13	99.4	91.1	95.4

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLE
AND ILLUSTRATIONS

TABLE 5. EFFECT OF H_2SO_4 CONCENTRATION ON CAPTURE EFFICIENCY

DROPPED
HEAD
BEGIN
SECTION
HERE

H_2SO_4 Conc. (ppm)	No. of Runs	% H_2SO_4 Capture		
		Max.	Min.	Avg.
1	6	99.2	92.0	95.0
5	4	99.4	94.7	97.8
20	1	95.9	95.9	95.9
50	2	91.7	91.1	91.4

Quartz Filter Holder

The results of tests to determine the effect of the quartz filter assembly held above $260^\circ C$ ($500^\circ F$) upon the passage of H_2SO_4 are recorded in Table 6. A comparison of the tests with and without filter support assembly indicates that there was no significant loss of H_2SO_4 in the filter assembly, and most of the variability was in the sampling and analytical technique itself.

Filter Holder H_2SO_4 Losses When Filter Was Preloaded with Particulate

The data in Table 7 show a summary of the tests to determine H_2SO_4 losses in the filter holder when the filters were preloaded with particulate samples from different recovery furnaces. During the tests the amount of particulate on the filters was equivalent to that which would be captured by pulling gas sample containing .2 g particulate/dscm (0.088 grains/dscf) at a rate of 8 lpm for 30 minutes. The results show large variations in H_2SO_4 loss in the particulate holder with the average losses varying from .5 to 3.8 ppm. The particulate samples were analyzed also for their alkalinity, measured as equivalent calcium carbonate, to determine if the filter losses could be correlated with the alkalinity of the particulate. However, no such correlation was observed (Table 7).

Filter Holder H_2SO_4 Losses When Filter Was Continuously Loaded with Particulate

H_2SO_4 Losses in Blank Runs--

BEGIN
LAST LINE
OF TEXT

Since a reference stream was analyzed to determine the H_2SO_4 concentration in the gas passing through the quartz filter, daily blank runs were made to determine the accuracy of the test procedure. The concentration of H_2SO_4 used in

BOTTOM OF
IMAGE AREA,
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUS-
TRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP LINE
IMAGE
AREA

TABLE 6. EFFECT OF QUARTZ FILTER ASSEMBLY UPON SAMPLE RECOVERY

No. of Runs	Ref. Train H_2SO_4 Conc. Range (ppm)	Filter Assembly Present	Percent Error*		
			Max.†	Min.‡	Avg.§
9	5.8-18.2	No	11.4	1.7	0.0
12	5.6-18.0	Yes	14.9	1.8	1.8

$$* \% \text{ Error} = \frac{\text{Ref. Train } H_2SO_4 \text{ Conc.} - \text{Sample Train } H_2SO_4 \text{ Conc.}}{\text{Ref. Train } H_2SO_4 \text{ Conc.}} \times 100$$

$$† \text{Max. Error} = \text{Max. Abs. } (\% \text{ Error})$$

$$‡ \text{Min. Error} = \text{Min. Abs. } (\% \text{ Error})$$

$$§ \text{Avg. Error} = \text{Abs. } (\Sigma (\% \text{ Error}) / \text{No. Runs})$$

TABLE 7. FILTER HOLDER LOSSES FOR DIFFERENT PARTICULATE SAMPLES

Source	Particulate Alkalinity, (g) $CaCO_3$ /kg	No. of Runs	H_2SO_4 Loss*					
			Max. ppm	Min. ppm	Avg. ppm	Max. ppm	Min. ppm	Avg. ppm
A	32.4	7	13	1.2	2	0.1	7	0.5
B	9.4	1	27	0.8	27	0.8	27	0.8
C	45.0	3	62	4.2	45	3.3	55	3.8
D	39.0	12	62	4.9	29	1.0	48	2.9
E	0	3	38	1.67	23	1.0	32	1.3
F	8.4	4	38	2.2	3	0.1	15	0.9
G	6.3	1	19	2.5	19	2.5	19	2.5

$$* H_2SO_4 \text{ Loss, } \% = \frac{(H_2SO_4 \text{ Conc. In} - H_2SO_4 \text{ Conc. Out})}{H_2SO_4 \text{ Conc. In}} \times 100$$

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLU-
STRATIONS

1/8"

DESIGN
LINE OR
TEXT

DESIGN
HEAD
BELOW
SECTION
LINE

these tests ranged from 5.3 ppm to 31.1 ppm, and the moisture content of the gas stream was approximately 10 percent. The results of the tests are recorded in Appendix C and are summarized in Table 8. A negative loss (Table 8) indicates that the H_2SO_4 concentration measured in the sample train was higher than the concentration of H_2SO_4 in the reference train. The data show that during the 19² blank runs, the error ranged from a loss of 2.3 ppm to a gain of 0.7 ppm with an average H_2SO_4 loss of 0.8 ppm. As a percent of inlet H_2SO_4 concentration, the mean error was 4 percent with a standard deviation of 5 percent.

H_2SO_4 Losses in Tests with Na_2SO_4 and Na_2CO_3

The results of three tests in which Na_2SO_4 particulate generated from Reagent Grade Na_2SO_4 were added to the sample gas stream are recorded in Table 9. The -2 percent mean error for the measurements is within the accuracy of tests and shows no loss of H_2SO_4 in passing through the quartz filter maintained above 260°C (500°F) in the presence of Na_2SO_4 .

Since Na_2CO_3 is usually present in recovery furnace particulate, tests were also run with particulate generated from Na_2CO_3 and mixtures of Na_2CO_3 and Na_2SO_4 . Reagent grade Na_2CO_3 and Na_2SO_4 were used. The results of the tests are recorded in Table 10. The ratios of Na_2SO_4 and Na_2CO_3 were 80 to 20 in runs 3 and 4 and 85 to 15 in runs 5 through 8.

At the end of each test the filter was also analyzed for sodium to determine the concentration of particulate in the gas stream during sampling. The concentration of total sodium, which was present as either Na_2SO_4 or as Na_2CO_3 in the gas stream, ranged from 0.029 to 0.050 g Na/1000 liters gas sample during these tests.

TABLE 8. RESULTS OF BLANK RUNS THROUGH QUARTZ FILTER HOLDER

Degree of H_2SO_4 Loss	ppm	Percent
Average	0.8	4
Standard Deviation	0.8	5
Maximum	2.3	15
Minimum	-0.7	-6

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

TABLE 9. H_2SO_4 LOSSES IN TESTS WITH Na_2SO_4

Degree of H_2SO_4 Loss	ppm	Percent
Mean	-0.3	-2
Maximum	0.1	1
Minimum	-0.5	-4

The data in Table 10 show that the H_2SO_4 losses during these tests were generally lower than were predicted based on the neutralization of all the Na_2CO_3 present with the particulate.

TABLE 10. H_2SO_4 LOSSES IN TESTS WITH
 Na_2CO_3 AND $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$

Run No.	Particulate	H_2SO_4 Conc., ppm	Na Conc., gm Na/ m ³	H_2SO_4 Loss, %		
				Observed	Possible*	Diff.**
1	Na_2CO_3	12.5	0.033	87	100	-13
2	"	10.0	0.029	100	100	0
3	$\text{Na}_2\text{CO}_3 +$	10.7	0.050	39	68	-29
4	Na_2SO_4	14.3	0.045	42	45	-3
5	"	14.7	0.041	22	28	-6
6	"	14.8	0.044	31	30	1
7	"	21.1	0.046	-7	22	-29
8	"	35.3	0.039	14	11	3

*If all Na_2CO_3 neutralized.

**Difference = H_2SO_4 loss observed, % - H_2SO_4 loss possible, %.

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLU-
STRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

H₂SO₄ Losses in Tests With Salt Cakes From Recovery Furnaces

DROPPED
HEAD
BEGIN
SECTIONS
HERE

The results of laboratory tests with salt cakes from recovery furnaces are recorded in Table 11. These data show substantially higher losses of H₂SO₄ than were expected based upon the alkalinity of the particulate, and may be due to the adsorption of H₂SO₄ on the particulate surface. The absolute values of H₂SO₄ losses were, however, low and, for purposes of estimating emission levels from kraft recovery furnaces, of little significance.

SO₂ CAPTURE EFFICIENCY OF GREENBURG-SMITH IMPINGERS

The results of the tests to determine the efficiency of capture of SO₂ in Greenburg-Smith impingers are summarized in Table 12. These data show that in the range of flow rates used no SO₂ reached the third impinger. Consequently, in all the subsequent work only two Greenburg-Smith impingers in series were used to capture SO₂ from gas streams.

TABLE 11. H₂SO₄ LOSSES IN TESTS WITH RECOVERY PARTICULATE

H ₂ SO ₄ Conc., ppm	H ₂ SO ₄ Loss,		H ₂ SO ₄ Loss*		Difference	
	ppm	Percent	ppm	Percent	ppm	Percent
20.0	3.4	17	1.4	7	2.0	10
23.0	6.0	26	1.6	7	4.4	19
28.8	4.3	15	1.4	5	2.9	10
32.3	0.3	1	1.0	3	-0.7	-2
8.8	1.4	16	3.1	35	1.7	-19
11.1	4.1	37	3.2	29	0.9	8
22.2	2.4	11	0.7	3	1.7	8
19.4	2.7	14	0.6	3	2.1	11
17.7	2.5	14	0.5	3	2.0	11

* If all alkalinity present was neutralized.

BEGIN
LAST LINE
OF TEXT

3/8"

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

TABLE 12. SO₂ CAPTURE EFFICIENCY OF
GREENBURG-SMITH IMPINGERS

Run No.	Flow Rate, lpm	SO ₂ Concentration, ppm	
		1 + 2 impinger	3 impinger
1	6.4	102	0
2	7.2	310	0
3	8.1	217	0
4	8.4	263	0
5	8.9	352	0

TESTS WITH ELECTROSTATIC PRECIPITATOR FILTER IN
SO₃/H₂SO₄ SAMPLING TRAIN

During the conduct of laboratory tests, it became clear that the alkaline particulate, which are contained in kraft recovery stack gas and collect on the quartz filter paper during sampling, offered a potential for SO₃/H₂SO₄ loss from the sample. To minimize the contact between the gas and the particulate and to reduce the potential for SO₃/H₂SO₄ loss, tests were conducted with two electrostatic precipitator (ESP) filters to determine if they offered any advantage over quartz filters.

The first ESP tested was obtained from the Southern Research Institute (SRI). This precipitator was built by SRI under EPA Contract 68-02-2131. The precipitator, however, failed during the laboratory tests when moisture was added to the sample stream.

The second precipitator shown in Figure 10 was obtained from James E. Cheney of EPA, Environmental Sciences Research Laboratory. The design and use of the precipitator has been fully described in a paper by Cheney, Walter and Homolya (13). When the precipitator was tested in the field on a kraft recovery furnace following an electrostatic precipitator, the efficiency was determined to be 99.3 percent at 10 lpm which was considered satisfactory. The unit was then tested in the laboratory to determine if there was any oxidation of SO₂ to SO₃ when it passed through the ESP, which was maintained above 500°F. The results of the tests (Table 13) show that there was no conversion of SO₂ to SO₃ in the ESP even when salt cake was present in the gas stream.

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD,
BEGIN
SECTIONS
HERE

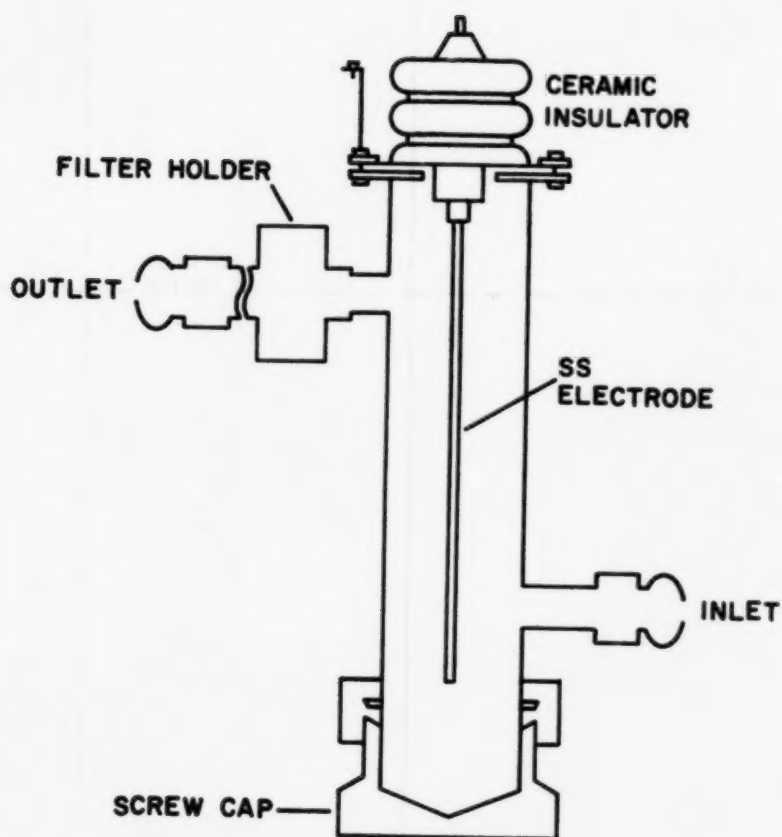


Figure 10. Electrostatic precipitator.

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

3/8"

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD
BEGIN
SECTION
HERE

TABLE 13. OXIDATION OF SO_2 TO SO_3 IN ELECTROSTATIC PRECIPITATOR

No.	Flow Rate, lpm	SO_2 Concentration, ppm	$\text{SO}_3/\text{H}_2\text{SO}_4$ Concentration, ppm
1	10.4	36	0
2	7.6	39	0
3	8.5	439	0
4	9.0*	347	0

*Salt cake present in the gas stream.

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUS-
TRATIONS

3/8"

SECTION 8

FIELD MEASUREMENTS OF SO_x EMISSIONS

The SO_x emissions from five kraft recovery furnaces located in the Southeast were measured. The furnaces chosen may be considered representative of a typical cross section of recovery furnaces presently in use in the kraft industry. All the samples were collected after the particulate control device to minimize particulate interference with SO_x measurement. This section describes the sources sampled, equipment used in the sampling train, sampling procedure, and the results of field tests.

SOURCES SAMPLED

Recovery Furnace A

Recovery furnace A was a Combustion Engineering kraft recovery furnace rated at 59,000 kg/hr (130,000 lb/hr) of steam. The furnace was equipped with a conventional cascade evaporator and two wet-bottom precipitators in series. Oxidized black liquor was fired in the furnace at 61 percent solids and sulfide levels below 0.5 gm/l as Na₂S. The stack gas containing 32 percent moisture was at 150°C and contained approximately 0.5 g particulate/dscm.

Recovery Furnace B

Recovery furnace B was a Babcox and Wilcox unit rated at 313,000 kg/hr (690,000 lb/hr) steam. The furnace had a direct contact evaporator and an electrostatic precipitator for particulate control. Oxidized black liquor, with less than 0.1 g Na₂S/l and 65 percent solids, was fired into the furnace. Liquor sulfidity was generally maintained around 30 percent. The stack gases leaving the precipitator were at approximately 145°C and contained 33 percent moisture and less than 0.1 g/dscm particulate.

Recovery Furnace C

Recovery furnace C was a Combustion Engineering kraft recovery unit rated at 186,000 kg/hr (410,000 lb/hr) steam. The furnace had no direct contact evaporation, and a dry-bottom precipitator was used for particulate control. Liquor was

fired at 66 percent solids, and the process sulfidity was maintained around 28 percent. The stack gas temperature was 180°C, the moisture content around 23 percent, and the particulate concentration below 0.3 g/dscm.

Recovery Furnace D

Recovery furnace D was a Combustion Engineering unit rated at 352,000 kg/hr (775,000 lb/hr) steam. During the tests the furnace was operated near its rated capacity. Black liquor solids content and liquor sulfidity were generally maintained at 65 percent and 26 percent, respectively. Recovery furnace D had no direct contact evaporator, hence the flue gas did not come in contact with black liquor. An electrostatic precipitator with a dry bottom was used for particulate control. The flue gas temperature was 160 to 170°C, moisture content was around 14 percent, and the particulate concentration was less than 0.1 g/dscm.

Recovery Furnace E

Recovery furnace E was a B&W cross-recovery furnace rated at 227,000 kg/hr (500,000 lb/hr) steam. Around 30 percent of the liquor fired in the furnace was from the sodium based semichemical cooking process. The liquor was fired at 65 percent solids, and 30 percent sulfidity was generally maintained. The furnace had no direct contact evaporator, and an electrostatic precipitator was used for particulate control. The flue gas temperature was 210°C, and it contained approximately 30 percent moisture and less than 0.1 g/dscm particulate.

SO_x SAMPLING TRAIN WITH QUARTZ FILTER

The sampling train used in SO_x sampling is shown in Figure 11. It consisted of a heated probe, quartz filter holder, SO₃ condenser, three Greenburg-Smith impingers in series, a column of silica gel, vacuum pump, rotameter, a dry gas meter, thermocouples, a digital thermometer, heating mantles, and a sampling box.

Heated Sampling Probe

The sampling probe was a 200-cm long 12-mm ID quartz tube with a heating element and a stainless steel jacket. A thermocouple was taped on the quartz tube and was insulated with glass wool and additional tape to accurately measure the probe temperature (special order, Scientific Glass).

Quartz Filter Holder

The quartz filter holder was fabricated locally as described earlier (special order, Southern Scientific, Micanopy, Florida).

BEGIN
FIRST
LINE OF
TEXT
HERE

DROPPED
HEAD;
BEGIN
SECTIONS
HERE

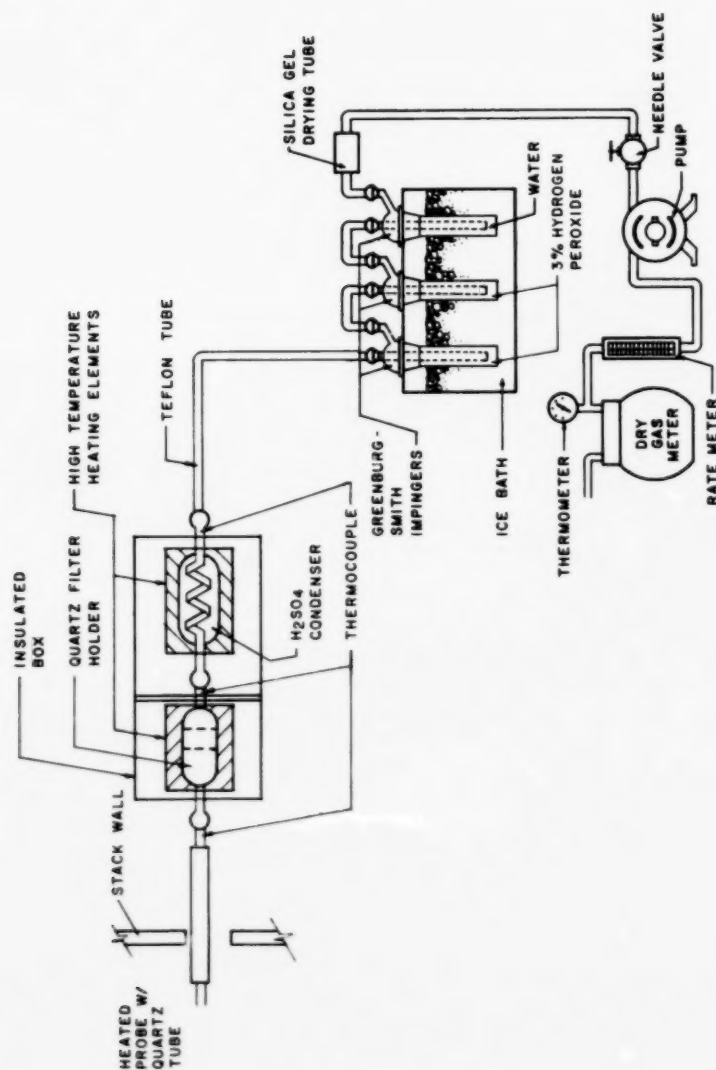


Figure 11. SO_x sampling train.

BEGIN
LAST LINE
OF TEXT

REPEATABLE
SCALE AREA
OUTSIDE
CONTOUR
FOR ANALYSIS
AND CALIBRATION

Tissuequartz filter papers with a 37-mm diameter were used in the filter holder (Pallflex Corporation).

SO₃ Condenser

The modified Graham condenser with a Type-C glass frit and 200 cm of 5-mm ID coil was fabricated locally (Southern Scientific).

Greenburg-Smith Impinger

Two 500-ml Greenburg-Smith impingers and a 500-ml Greenburg-Smith modified impinger were used in series. The first two impingers contained 100 ml each of 3 percent hydrogen peroxide, while the third impinger was empty. All impingers were kept in an ice bath. The impingers were connected to the SO₃ condenser with a 200 cm long 9.6 mm (3/8") diameter Teflon tube.

Digital Thermometer and Thermocouples

A portable digital thermometer (Bailey Instruments, Model BAT-8) and copper and constantan thermocouples (Bailey Type TW26, TW36) were used to measure temperatures.

Heating Mantles

High temperature cylindrical heating mantles were used to heat the quartz filter holder and the SO₃ condenser (special order, Ace Glass Co.).

Sampling Box

The sampling box was made of aluminum and was designed to slide on a monorail. The probe was mounted on the sampling box. The quartz filter holder and the SO₃ condenser were located inside the box.

The indicating silica gel, vacuum pump, and dry gas meters were standard equipment used in particulate sampling trains.

SO_x SAMPLING TRAIN WITH ELECTROSTATIC PRECIPITATOR

The sampling train was the same as shown in Figure 11, except that the heated quartz filter was replaced with the electrostatic precipitator (13). The precipitator was maintained above 260°C (500°F). This equipment has been described in the previous section.

TEST PROCEDURE

The equipment was cleaned and assembled as shown in Figure 11. One hundred milliliters ml of 3 percent hydrogen peroxide was poured into each of the first two Greenburg-Smith

impingers. A leak check was made on the sampling train, and if any leaks were found, they were corrected. The probe was inserted into the stack, and heat to the probe, the quartz filter, and the SO_3 condenser was turned on. After the desired temperatures were reached, the vacuum pump was started and the stack gas was sampled for 30 minutes. At the end of the sampling period the pump was stopped, the probe was carefully withdrawn from the stack, and the system was allowed to cool down. The probe, the quartz filter holder, and the SO_3 condenser were separately washed with deionized water using multiple rinses to ensure good washing. The rinse solutions and the impinger solutions were collected and taken to the laboratory where the probe and filter wash were analyzed for sodium and the condenser wash and impinger solutions for sulfate. Details of the analytical procedure are described in Appendix A. Figure 12 shows a typical data sheet that may be used during such a test.

The stack gas temperatures during field tests were much higher than the estimated dewpoint of H_2SO_4 , and H_2SO_4 was expected to be present in vapor phase only. Consequently, it was determined that neither isokinetic sampling nor a stack traverse were required during these tests. Also, since laboratory studies had shown that even small amounts of particulate interfered with $\text{SO}_3/\text{H}_2\text{SO}_4$ measurement, a straight probe placed at right angles to the direction of gas flow was used to reduce the amount of particulate entering the probe and filter. The use of an oxygen analyzer on the gases leaving the dry gas meter minimized the concern for gas stratification in the stack or leaks in the sampling system, though attempts were always made to eliminate any leaks present in the sampling train.

SO_x EMISSION DATA

The SO_x concentrations in the five tested kraft recovery furnaces are described below. It should be noted that the SO_2 and $\text{SO}_3/\text{H}_2\text{SO}_4$ concentrations have also been corrected to 8 percent oxygen concentration, the level specified by the New Source Performance Standards for reporting gaseous emissions from kraft recovery furnaces to provide a common basis for comparing the results. The reported oxygen levels were the concentrations measured in the sample stream and generally represent the stack gas oxygen content.

The SO_x emission data from Recovery Furnace A are tabulated in Table 14.^x In the five tests, the range of $\text{SO}_3/\text{H}_2\text{SO}_4$ concentration corrected to 8 percent oxygen was from 0⁴ (less than measurable) to 0.91 ppm with a mean of 0.31 ppm. The SO_2 concentrations varied from 132 to 245 ppm, for an average of 146 ppm.

Table 15 contains the results of five tests on Recovery Furnace B. The condenser wash for run no. 3 was lost, hence no

BEGIN FIRST LINE OF TEXT HERE

 DROPPED HEAD WIDTH SECTION HERE

TYPING GUIDE SHEET

CENTER OF PAGE

 TOP OF IMAGE AREA

Source _____

Date _____

Run # _____

Furnace Load _____

Stack Gas Temp. _____

Atmospheric Pressure _____

Final Dry Gas Meter Reading _____

Initial Dry Gas Meter Reading _____

Volume Sampled _____

Time (Min)	Temperature, °F			
	Probe	Filter	Condenser	Dry Gas Meter In Out
0				
5				
10				
15				
20				
25				
30				

Figure 12. SO₃ measurement field data sheet.

BEGIN LAST LINE OF TEXT

 3 1/8"

36
PAGE NUMBER

BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

EPA-207 (CAL) (5-70)

TABLE 14. RECOVERY FURNACE A SO_x DATA

Date	Run No.	% Oxygen	H ₂ SO ₄ ppm	SO ₂ , ppm	Conc. Corrected to 8% Oxygen	
					H ₂ SO ₄ , ppm	SO ₂ , ppm
1/30/79	1	6.3	0.15	132	0.13	117
1/30/79	2	6.9	0.40	137	0.33	112
1/31/79	3	6.3	0*	245	0*	216
1/31/79	4	5.3	1.10	170	0.91	141
1/31/79	5	5.8	0.19	170	0.16	145

*Less than measurable.

H₂SO₄ data can be reported for that run. The data show SO₃/H₂SO₄ levels of 0 to 0.29 ppm with an average of 0.16 ppm, and SO₂ levels of 10.3 to 24.0 ppm with a mean of 14.0 ppm.

Four tests were conducted on recovery furnace C, and the SO_x emission measurements are recorded in Table 16. A quartz filter holder was used in the first three tests for particulate separation. The fourth test was made with the electrostatic

TABLE 15. RECOVERY FURNACE B SO_x DATA

Date	Run No.	% Oxygen	H ₂ SO ₄ ppm	SO ₂ , ppm	Conc. Corrected to 8% Oxygen	
					H ₂ SO ₄ , ppm	SO ₂ , ppm
2/22/79	1	4.0	0.26	10.3	0.20	7.9
2/22/79	2	4.3	0.37	13.8	0.29	10.7
2/22/79	3	4.5	-	18.9	-	14.9
2/22/79	4	5.0	0*	17.6	0*	15.2
2/22/79	5	6.5	0.15	24.0	0.13	21.5

*Less than measurable.

precipitator and a stainless steel filter holder with quartz filter in the sampling train to remove particulate from the gas stream. Only one test was made with the precipitator because the precipitator failed after the test and had to be brought back to the laboratory. The $\text{SO}_3/\text{H}_2\text{SO}_4$ concentrations in these tests varied from 0.21 to 0.91 ppm, with an average value of 0.62 ppm. The range of SO_2 concentrations was 163 to 421 ppm, and the mean was 316 ppm.

The results of nine runs on Recovery Furnace D are summarized in Table 17. The condenser wash for determining H_2SO_4 concentration was lost for run no. 1. Runs 1 to 6 were made with the quartz filter holder for particulate separation. During runs 7, 8, and 9 the electrostatic precipitator was used in the sampling train for particulate separation. The data show maximum, minimum, and average $\text{SO}_3/\text{H}_2\text{SO}_4$ concentrations of 2.98, 0.17, and 1.36 ppm, respectively. The range of SO_2 concentrations was 199 to 445 ppm, with a mean value of 341 ppm.

Table 18 shows the results of five SO_x measurements on Recovery Furnace E. The range of $\text{SO}_3/\text{H}_2\text{SO}_4$ concentrations was from 0.49 to 1.71 ppm, and the average value was 0.97 ppm. The SO_2 concentration varied from 405 to 739 ppm, and the mean was 496 ppm.

DISCUSSION

During this study kraft recovery furnaces with a DCE and furnaces without a DCE were sampled, and two slightly different $\text{SO}_3/\text{H}_2\text{SO}_4$ sample conditioning techniques were used on non-DCE

TABLE 16. RECOVERY FURNACE C SO_x DATA

Date	Run No.	% Oxygen	H_2SO_4 ppm	SO_2 , ppm	Conc. Corrected to 8% Oxygen	
					H_2SO_4 , ppm	SO_2 , ppm
4/24/79	1	9.8	0.18	141	0.21	163
4/24/79	2	10.1	0.38	219	0.45	261
4/24/79	3	10.6	0.72	336	0.90	420
4/25/79	4*	16.1	0.34	157	0.91	421

*Electrostatic precipitator used in the sampling train.

TABLE 17. RECOVERY FURNACE D SO_x DATA

Date	Run No.	% Oxygen	H ₂ SO ₄ ppm	SO ₂ , ppm	Conc. Corrected to 8% Oxygen	
					H ₂ SO ₄ , ppm	SO ₂ , ppm
5/8/79	1	4.7	-	432	-	344
5/8/79	2	11.1	2.00	257	2.63	338
5/8/79	3	6.0	1.70	514	1.47	445
5/8/79	4	4.9	0.31	467	0.25	376
5/8/79	5	4.9	0.21	448	0.17	361
5/8/79	6	5.3	0.92	484	0.76	401
5/9/79	7*	4.7	1.24	413	0.99	329
5/10/79	8*	4.1	3.88	355	2.98	272
5/10/79	9*	4.1	2.07	259	1.59	199

*Electrostatic precipitator used in the sampling train.

TABLE 18. RECOVERY FURNACE E SO_x DATA

Date	Run No.	% Oxygen	H ₂ SO ₄ ppm	SO ₂ , ppm	Conc. Corrected to 8% Oxygen	
					H ₂ SO ₄ , ppm	SO ₂ , ppm
2/7/79	1	4.5	2.18	532	1.71	418
2/7/79	2	4.5	0.62	606	0.49	477
2/7/79	3	4.6	1.57	558	1.24	442
2/7/79	4	4.7	0.99	508	0.79	405
2/7/79	5	4.9	0.80	916	0.64	739

furnaces. Accordingly, the data on $\text{SO}_3/\text{H}_2\text{SO}_4$ emissions have been further summarized in Table 19 according to the types of furnaces sampled as well as the sample conditioning techniques. The data for all the tests show a $\text{SO}_3/\text{H}_2\text{SO}_4$ concentration range of 0 to 2.98 ppm, with an average value of 0.81 ppm. When the observations are separated according to the types of kraft recovery furnaces, they exhibit an average $\text{SO}_3/\text{H}_2\text{SO}_4$ concentration of 0.24 ppm in stack gases from furnaces with DCE and a slightly higher concentration of 1.07 ppm in stack gases from non-DCE furnaces. The observed average flue gas SO_2 concentration of 356 ppm in non-DCE furnaces was also substantially higher than the average SO_2 concentration of 80 ppm in furnaces with DCE.

The data in Table 19 on non-DCE furnaces indicate that the 0.90 ppm average $\text{SO}_3/\text{H}_2\text{SO}_4$ level measured when a quartz filter was used in the sampling train was lower than the 1.62 ppm $\text{SO}_3/\text{H}_2\text{SO}_4$ concentration when a miniature electrostatic precipitator (ESP) was used in the sampling train for particulate separation. These differences are too small to be of any importance and may be due to (a) source variability, since the two trains were not run simultaneously, (b) oxidation of SO_2 to SO_3 in the ESP during sampling, or (c) lower losses of $\text{SO}_3/\text{H}_2\text{SO}_4$ in the ESP.

The lower SO_2 concentrations in recovery furnaces with a DCE were expected and are generally due to SO_2 scrubbing in the DCE.

In order to determine if there was any linear correlation between the $\text{SO}_3/\text{H}_2\text{SO}_4$ and the SO_2 concentrations, the values of coefficient of correlation (r) between $\text{SO}_3/\text{H}_2\text{SO}_4$ and SO_2 were

TABLE 19. $\text{SO}_3/\text{H}_2\text{SO}_4$ EMISSION DATA SUMMARY

Samples	No.	$\text{SO}_3/\text{H}_2\text{SO}_4$ Conc., ppm			SO_2 Conc., ppm
		Max.	Min.	Avg.	
All Samples	26	2.98	0	0.81	260
Type of Furnaces					
-DCE Furnaces	9	1.10	0	0.24	80
-non-DCE Furnaces	17	2.98	0.17	1.07	356
Non-DCE Furnaces					
-Quartz Filter Only	13	2.63	0.17	0.90	430
-ESP Only	4	2.98	0.91	1.62	305

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD;
BEGIN
SECTIONS
HERE

determined for each recovery furnace and are tabulated in Table 20. These results show that except for recovery furnace C, for which there was a perfect correlation between $\text{SO}_3/\text{H}_2\text{SO}_4$ and SO_2 , there was very poor correlation between $\text{SO}_3/\text{H}_2\text{SO}_4$ and SO_2 .

As a result, it may be stated that if a particular kraft recovery furnace stack gas has a high level of SO_2 , one should not infer without any tests that it also emits a high concentration of $\text{SO}_3/\text{H}_2\text{SO}_4$.

To understand the relative significance of the SO_2 levels in kraft recovery furnace stack gases, it is important^x to compare these emissions to these observed oil- or coal-fired utility or industrial boilers. Some of the recently published SO_2 and H_2SO_4 emission data from oil- and coal-fired boilers are summarized in Table 21. These data show that both the SO_2 and the H_2SO_4 concentrations in flue gases from oil- and coal-fired boilers are much higher than the levels in kraft recovery furnace stack gases.

TABLE 20. COEFFICIENT OF CORRELATION
BETWEEN $\text{SO}_3/\text{H}_2\text{SO}_4$ AND SO_2

Recovery Furnace	Coefficient of Correlation
A	-0.33
B	-0.50
C	0.99
D	-0.42
E	-0.46

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE ARE
OUTSIDE
DIMENSION
FOR TABLE
AND ILLUSTRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

TABLE 21. SO_x EMISSIONS FROM OIL- AND COAL-FIRED
UTILITY AND INDUSTRIAL BOILERS

DROPPED
HEAD
BEGIN
SECTIONS
HERE

Authors	Fuel Sulfur Content, %	SO ₂ , ppm	H ₂ SO ₄ , ppm
Howes ⁽¹⁶⁾	2.5-3.8	1,300-3,300	5-46
Doyle ⁽¹⁷⁾	2.3	-	2-42
Homolya ⁽¹⁴⁾	1.0-2.4	-	9-25
Bailey ⁽¹⁵⁾	-	2,800-3,500	1-30

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD,
BEGIN
SECTIONS
HERE

REFERENCES

- (1) Hillenbrand, L. J., R. B. Engdahl, and R. E. Barrett. Chemical Composition of Particulate Air Pollutants from Fossil-Fuel Combustion Sources. Battelle Columbus Laboratories, II-2 (March 1, 1973).
- (2) Yost, D. M. and H. Russell, Jr. Systematic Inorganic Chemistry. Prentice-Hall, Inc., N. Y., (1946), 336 pp.
- (3) Lundgren, D. A. and T. C. Gunderson. Filtration Characteristics of Glass Fiber Filter Media at Elevated Temperatures. EPA/2-76-192, U. S. Environmental Protection Agency, July 1976.
- (4) Thomas, J. S., and W. F. Barker. The Partial Pressure of Water Vapor and of Sulfuric Acid Over Concentrated Solutions of Sulfuric Acid at High Temperatures. J. Chem. Soc., London, 127 pp., (1925).
- (5) Abel, E. The Vapor Phase Above the System Sulfuric Acid-Water. J. Phys. Chem., 50, 260 (1946).
- (6) Greenwalt, C. H. Partial Pressure of Water Out of Aqueous Solutions of Sulfuric Acid. Ind. and Eng. Chem., Vol. 17, pp. 522-523.
- (7) Gmitro, J. I. and T. Vermuelen. Vapor-Liquid Equilibria for Aqueous Sulfuric Acid. Univ. of Cal. Radiation Lab., Report 10866, Berkeley, Cal. (June 24, 1963).
- (8) Martin, R. R. The Effect of Water Vapor on the Production of Sulfur Trioxide in Combustion Processes. Ph.D. Dissertation, Univ. of Tulsa, Okla. (1971).
- (9) Verhoff, F. H. and J. T. Banchero. Predicting Dewpoints of Flue Gases. CEP, 70, (8), 1974.
- (10) Goksoyr, H. and K. Ross. The Determination of Sulfur Trioxide in Flue Gases. J. Inst. Fuel, 35, 177, 1962.
- (11) Maddalone, R. F. Process Measurement Procedures Sulfuric Acid Emissions. TRW Systems, EPA Contract No. 68-02-2165, Task No. 13 (February 1977).

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUS-
TRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD
BEGIN
SECTIONS
HERE

- (12) EPA Revised Reference Methods 1-8 at 42 FR 41754, August 18, 1977, Effective September 19, 1977.
- (13) Cheney, J. L., Walter, C., Homolya, J. B. Application of an Electrostatic Precipitator for Instrumental Sampling of Sulfuric Acid. Analytical Letters, 12(A7):783-801, 1979.
- (14) Homolya, J. B., J. L. Cheney. An Assessment of Sulfuric Acid and Sulfate Emissions from the Combustion of Fossil Fuels. Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources. Volume 2. EPA-600/9-78-020b, U.S. Environmental Protection Agency, August 1978.
- (15) Bailey, E. M., H. A. Ruddock. Measurement of Sulfur Trioxide at Tennessee Valley Authority Coal-Fired Power Plants Using the Condenser Method. Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources. Volume 1. EPA-600/9-78-020a, U. S. Environmental Protection Agency, August 1978.
- (16) Howes, J. E., Jr. Sulfur Oxide Measurements of Utility Power Plant Emissions. Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources. Volume 2. EPA-600/9-78-020b, U. S. Environmental Protection Agency, August 1978.
- (17) Doyle, B. W. and R. C. Booth. Some Recent Data on SO₃ and SO₄ Levels in Utility Boilers. Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources. Volume 2. EPA-600/9-78-020b, U. S. Environmental Protection Agency, August 1978.

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUS-
TRATIONS

3/8"

APPENDIX A

METHODS OF SULFATE ANALYSIS

SULFATE ANALYSIS WITH DIMETHYLSULFONAZO III AS INDICATOR

The method of sulfate analysis with dimethylsulfonazo III indicator was reported by Scroggins (1). Our laboratory studies showed that it was difficult to always identify the titration end point change in color from mauve-purple to azure-blue. Consequently, this procedure was not used. The method of analysis is described below.

Reagents and Apparatus

- (a) Cation exchange resin - Dowex 50W-X8.
- (b) Barium perchlorate standard solution - Dissolve 4.0 g $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ in 1 liter water and adjust pH to 3.0 with 0.5N HCl.
- (c) Dimethylsulfonazo III indicator solution - Dissolve 100 mg dimethylsulfonazo III in 30 ml water. Elute solution through column of ion exchange resin, (a) (pretreated with 100 ml 3N HCl). Dilute eluate to 100 ml with water.
- (d) Titration lamp - Stirrer-lamp.

Standardization of Barium Perchlorate Solution

Accurately weigh 5-7 mg freshly dried K_2SO_4 and transfer to 200 ml tall-form graduated beaker. Dissolve in 50 ml water. Adjust pH to 3.0 ± 0.2 with ca 4 drops 0.5N HCl solution. Add 6 drops (0.3 ml) dimethylsulfonazo III indicator solution and 50 ml acetone. With vigorous stirring, titrate with 0.01M barium perchlorate solution to permanent sky blue which persists while stirring for >30 sec. Light blue may appear at start of titration but normal purple will return upon continued titration. Titration end point is permanent change from mauve-purple to azure-blue. Subtract reagent blank. Repeat standardization >3 times. Normality = $\text{mg } \text{K}_2\text{SO}_4 / (\text{mol. wt.} \times \text{ml barium perchlorate solution}) \times 2$.

Determination

Take 50 ml sample. Proceed as in standardization, beginning, "Adjust pH to 3.0 ± 0.2 ..." Subtract blank from volume used.

SULFATE ANALYSIS WITH THORIN AS INDICATOR

The method of sulfate analysis with Thorin as indicator has been described in EPA Reference Method 8 (12). The procedure is described below.

Reagents

Isopropyl alcohol, 100 percent. Hydrogen peroxide, 3 percent. Dilute 30 percent hydrogen peroxide 1:9 (v/v) with deionized water. Prepare fresh daily.

Thorin indicator. Dissolve 0.20 g in 100 ml of deionized water.

Barium Perchlorate Solution, .0100N. Dissolve 1.95 g of barium perchlorate trihydrate $[\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}]$ in 200 ml distilled water and dilute to 1 liter with isopropyl alcohol. Alternatively, 1.22 g of $[\text{BaCl}_2 \cdot 2\text{H}_2\text{O}]$ may be used instead of the perchlorate. Standardize.

Sulfuric Acid Standard, 0.0100N. Purchase or standardize against .0100N NaOH which has been standardized against potassium acid phthalate.

Sample AnalysisH₂SO₄ Samples--

The H₂SO₄ concentrations in kraft recovery furnace stack gases are generally so low that the entire sample may have to be used in titration. Transfer the sample into a 250 ml Erlenmeyer flask, add enough isopropyl alcohol to give a 80 percent isopropyl alcohol solution and two to four drops of Thorin indicator. Titrate to a pink end point using standard barium perchlorate solution. Run a blank. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is larger.

Barium Perchlorate Solution Standardization

Standardize the barium perchlorate solution against 25 ml of standard sulfuric acid to which 100 ml of 100 percent isopropyl alcohol has been added.

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD
BEGIN
SECTIONS
HERE

APPENDIX B

CALCULATIONS

The nomenclature and equations used in calculations are the same as in EPA Reference Method 8 (12). Only the equations for calculating concentrations in ppm have been added.

$C_{H_2SO_4}$ = Sulfuric acid concentration, g/dscm (lb/dscf)

$C_{H_2SO_4}$, ppm = Sulfuric acid concentration, ppm

C_{SO_2} = Sulfur dioxide concentration, g/dscm (lb/dscf)

C_{SO_2} , ppm = Sulfur dioxide concentration, ppm

N = Normality of barium perchlorate titrant, g equivalents/lit.

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg)

$P_{standard}$ = Standard absolute pressure, 760 mm Hg (29.92 in. Hg)

T_m = Average absolute dry gas meter temperature, °K (°R)

T_{std} = Standard absolute temperature, 293°K (528°R)

V_a = Volume of sample aliquot titrated (all for H_2SO_4 , 5-10 ml SO_2)

V_{soln} = Total volume of solution in which the sulfuric acid or sulfur dioxide sample is contained.

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf)

$V_{m(std)}$ = V_m corrected to standard conditions dscm (dscf)

V_t = Volume of barium perchlorate titrant used for the sample, ml

V_{tb} = Volume of barium perchlorate titrant used for the blank, ml

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA;
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

Y = Dry gas meter calibration factor

Calculations

$$V_{m(std)} = V_m Y \left(\frac{T_{std}}{T_m} \right) \left(\frac{P_{bar}}{P_{std}} \right)$$

$$C_{H_2SO_4} = \frac{K_2 N (V_t - V_{tb}) \left(\frac{V_{soln}}{V_a} \right)}{V_{m(std)}}$$

where:

$$K_2 = 0.04904 \text{ g/milliequivalent for } C_{H_2SO_4} \text{ in g/dscm} = 1.081 \times 10^4 \frac{\text{lb}}{\text{meq}} \text{ for } C_{H_2SO_4} \text{ in lb/dscf}$$

$$C_{H_2SO_4}, \text{ ppm} = 249 \times C_{H_2SO_4}$$

where: $C_{H_2SO_4}$ is in g/dscm

$$C_{SO_2} = \frac{K_3 N (V_t - V_{tb}) \left(\frac{V_{soln}}{V_a} \right)}{V_{m(std)}}$$

$$\text{where: } K_3 = 0.03203 \text{ g/meq for } C_{SO_2} \text{ in g/dscm} = 7.061 \times 10^{-5} \text{ lb/meq for } C_{SO_2} \text{ in lb/dscf}$$

$$C_{SO_2}, \text{ ppm} = 382 \times C_{SO_2}$$

where: C_{SO_2} is in g/dscm

Sample Calculations

Date 1/30/79 Source Recovery Furnace A Run No. 1

Dry Gas Meter Reading: Final = 354.468 ft³
Initial = 345.365 ft³
 $V_m = 9.063 \text{ ft}^3$

$P_{bar} = 29.98 \text{ Hg}$ $T_m = (70 + 460)^\circ R$

Y = 1.00

For H_2SO_4 : $V_{soln} = V_a = \text{All sample}$

$V_t = 0.1 \text{ ml}$ $V_{tb} = 0 \text{ ml}$

N = 0.0324N

For SO_2 : $V_{\text{soln}} = 100 \text{ ml}$, $V_a = 700 \text{ ml}$
 $V_t = 12.4 \text{ ml}$ $V_{tb} = 0 \text{ ml}$
 $N = .0324N$

Calculations

$$\begin{aligned} V_{m(\text{std})} &= 9.063 \times 1 \times \frac{528}{530} \times \frac{29.98}{29.92} \text{ ft}^3 \\ &= 9.047 \text{ ft}^3 \\ &= 9.047 \times 28.32 \times 10^3 \text{ mt}^3 \\ &= 256.208 \times 10^3 \text{ mt}^3 \end{aligned}$$

$$\begin{aligned} C_{\text{H}_2\text{SO}_4} &= \frac{0.04904 \times .0324 \times (9.1-0) \times 1}{256.208 \times 10^3} \\ &= .000620 \text{ gm/mt}^3 \end{aligned}$$

$$\begin{aligned} C_{\text{H}_2\text{SO}_4}, \text{ ppm} &= .000620 \times 249 \\ &= 0.15 \text{ ppm} \end{aligned}$$

$$\begin{aligned} C_{\text{SO}_2} &= \frac{0.03203 \times .0324 \times 12.4 \times \frac{700}{100}}{256.208 \times 10^3} \\ &= .3516 \text{ gm/mt}^3 \end{aligned}$$

$$\begin{aligned} C_{\text{SO}_2}, \text{ ppm} &= 382 \times .3516 \\ &= 134 \text{ ppm} \end{aligned}$$

BEGIN
FIRST
LINE OF
TEXT
HERE

TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD:
BEGIN
SECTION
HERE

APPENDIX C

H₂SO₄ LOSSES IN BLANK RUNS WITH
QUARTZ FILTER AND FILTER HOLDER IN LINE

Run No.	H ₂ SO ₄ Conc. In ppm	H ₂ SO ₄ Loss*, %
1	5.3	7
2	7.9	-9
3	5.4	4
4	18.7	8
5	18.6	10
6	20.6	0
7	21.8	8
8	25.9	4
9	12.5	15
10	13.3	0
11	17.4	-2
12	18.8	1
13	31.1	1
14	10.5	1
15	11.5	3
16	10.6	-6
17	18.7	4
18	19.1	12
19	21.5	8

*Mean Loss, % = 4

Standard Deviation, % = 6

$$\text{H}_2\text{SO}_4 \text{ Loss} = \frac{\text{H}_2\text{SO}_4 \text{ Conc., In} - \text{H}_2\text{SO}_4 \text{ Conc., Out}}{\text{H}_2\text{SO}_4 \text{ Conc., In}} \times 100$$

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA;
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUS-
TRATIONS

3/8"

50